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# REACTOR FUEL PROCESSING

*A Quarterly Technical Progress Review*

Prepared for U. S. ATOMIC ENERGY COMMISSION by ARGONNE NATIONAL LABORATORY

July 1959



● VOLUME 2

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# REACTOR FUEL PROCESSING

a review of recent developments prepared by

ARGONNE NATIONAL LABORATORY

JULY 1959

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## *foreword*

This quarterly review of *Reactor Fuel Processing* has been prepared at the request of the U. S. Atomic Energy Commission, Division of Information Services. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this broad field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review who are personnel of the Argonne National Laboratory, Chemical Engineering Division. Those taking part in the preparation of this issue are L. Burris, Jr., I. G. Dillon, A. A. Jonke, S. Lawroski, M. Levenson, W. J. Mecham, W. A. Rodger, J. H. Schraadt, W. B. Seefeldt, R. K. Steunenberg, and V. G. Trice. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

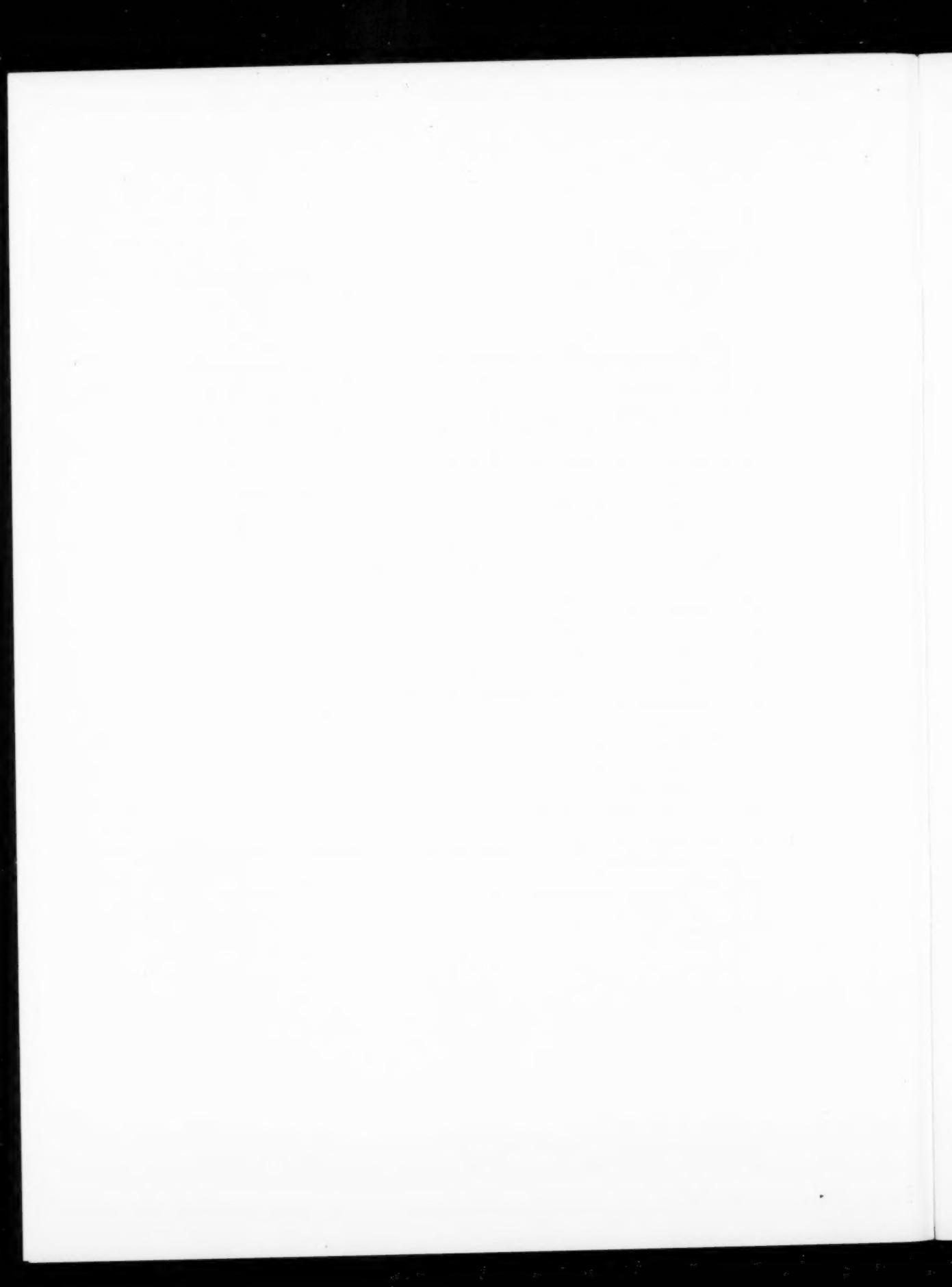
S. LAWROSKI

*Director, Chemical Engineering Division  
Argonne National Laboratory*

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# REACTOR FUEL PROCESSING

## COMMERCIAL ASPECTS OF FUEL PROCESSING

### Fuel Recovery Costs Analyzed

At the Nuclear Congress held in Cleveland in April 1959, Guthrie<sup>1</sup> gave an analysis of reprocessing costs as a function of plant size. Starting with the average cost for electricity from combustible sources in the United States (6.8 mills/kw-hr) and subtracting out the best that can be expected from other components of the fuel cycle, he arrived at a figure of 0.35 mill/kw-hr as the fuel recovery cost which must be achieved in order to have competitive nuclear power in the United States. His conclusions on the effect of plant size and loading on the radiochemical reprocessing cost are shown in Fig. 1. It may be concluded from this figure that, in order to reprocess fuels for 0.35 mill/kw-

hr (at 8000 Mwd/ton burn-up), a 6-ton per day plant operating at capacity would be required. This would require an installed nuclear capacity of 48,000 Mw (heat). The date at which such a plant could be built would depend on the nuclear power build-up. Build-up predictions put this somewhere between 1968 and 1973.

### New Base Charges for Pu and U<sup>233</sup>

On Dec. 3, 1958, the AEC announced base charges of \$15 per gram for U<sup>233</sup> and \$12 per gram for plutonium to be made available for research and development purposes to private individuals and companies in the United States and to foreign governments under agreements for cooperation.<sup>2</sup> The research and development activities referred to include critical experiments but exclude the use of these materials as fuel in nuclear reactors. As of now no private reactors are being planned or built which would require Commission lease of U<sup>233</sup> or plutonium for use as an energy source. It is hoped, however, that the base prices as now established will encourage development of the materials as nuclear fuels on a par with U<sup>235</sup>. The presidential allotment of these materials for domestic civilian use totals 3.6 kg of U<sup>233</sup> and 37.5 kg of plutonium. As of Sept. 20, 1958, allocations to domestic licensees amounted to 0.04 kg of U<sup>233</sup> and 12.12 kg of plutonium.

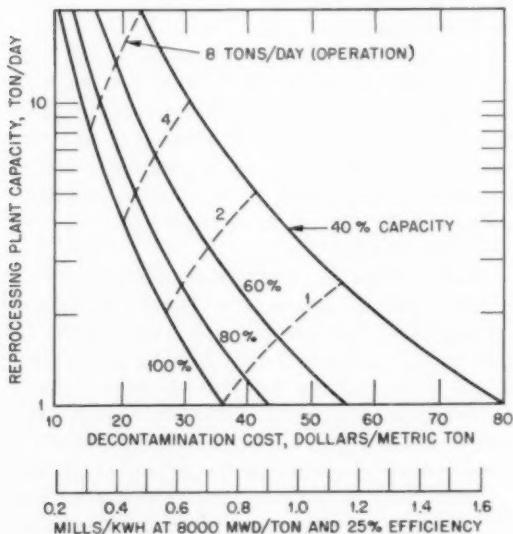


Figure 1—Effect of plant size and loading on radiochemical reprocessing cost.<sup>1</sup>

### AEC Releases Proposed Radiation

#### Exposure Standards

The AEC has approved the issuance for public comment of proposed regulator amendments to existing "Standards for Protection Against Radiation" which would put into effect for Commission licensees the latest recommendations of the National Committee on Radiation Protection and

Measurements (NCRP) concerning maximum permissible accumulated radiation exposures.<sup>3,4</sup>

A principal effect of the proposed amendments, based on recommendations of the NCRP published in April 1958 in an Addendum to National Bureau of Standards Handbook 59, would be to limit the life-time accumulated radiation doses of workers in restricted areas, where radiation levels are monitored and controlled, to approximately one-third of limits permitted under the existing regulation. The revision would limit the total external radiation exposure any worker beyond the age of 18 may accumulate to an average of 5 rem per year and not more than 12 rem in any one year. Present limits are 15 rem per year without further restrictions as to accumulated dose.

Maximum permissible concentrations of radioactive substances in air and water would also be revised to include latest NCRP recommendations on internal dose being published in a new National Bureau of Standards Handbook 69, as announced by NBS on Apr. 23, 1959. One of the changes relates to radioactive materials which have their principal effect on the whole body or gonads. In controlled areas, the maximum permissible concentrations of these materials would be reduced to approximately one-third of the concentration values previously specified for occupational exposures. For other radioisotopes, some values would be increased, some decreased, and others would remain essentially the same.

For individuals outside of controlled areas, and for all persons under 18 years of age, the maximum permissible radiation doses and concentrations in air and water would be one-tenth of the recommended permissible values for radiation workers.

### Specifications for Irradiated Fuel

#### Shipping Casks

In June 1958, at a nuclear fuels transportation meeting in Chicago, the AEC listed the reprocessing facilities that will be used for handling the irradiated fuels expected to be discharged, starting in 1961, from private nuclear power reactors.<sup>5</sup> Also discussed at that meeting were preliminary design specifications for irradiated fuel shipping casks. At a second Chicago meeting,<sup>6</sup> held in December 1958, the AEC spelled out its proposed licensing criteria for irradiated

fuel shipping containers.\* These criteria can be summarized as follows:

**Critical Mass.** To avoid the possibility of a critical mass reaction during transportation, the AEC proposes that (1) no more than three-quarters of the quantity of fuel required to be critical will be shipped in a single container, and (2) the quantity shipped will not exceed that necessary to yield a reactivity value of 0.8 per cent, whichever is larger. In both cases, it is to be assumed that the fuel is optimally spaced for maximum reactivity, that water fills all intervening and surrounding spaces, and that no artificial poisons are present.

**Heat Removal.** Prior to shipment, fuel elements must be stored long enough (on the order of 120 days) to assure that when the cask is loaded with fuel elements, the temperature will remain at least 100°C below that temperature which could result in rupture of the elements and release of fission products, without the aid of heat-transfer media other than air convection.

**Radiation Levels.** Gamma radiation shall not exceed 200 mr/hr at any readily accessible point on the surface of the container or 10 mr/hr at a distance of 3 meters from the surface of the container.

**External Contamination.** External contamination of the cask shall not exceed 0.5 mr/hr for beta-gamma and 500 disintegrations/min/100 sq cm for alpha.

**Structural Integrity.** The design of the container and materials of construction shall be such that the container shall maintain its structural integrity under all conditions of shipment and under conditions of severe impact and heat.

**Additional Criteria.** Under certain conditions shipments by water can be accepted at all but the Idaho site.

Casks must be readily removable from the shipping vehicle and must not exceed a maximum weight of 75 tons when loaded. Three of the reprocessing sites will unload casks under water while the fourth site will unload casks in air.

Since the cask primary coolant system should not ordinarily operate at pressure greater than atmospheric, an automatic pressure release system must be incorporated as well as methods of control or containment of the released fluid.

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\*Final form of the licensing criteria is being completed and will be available from the U. S. Atomic Energy Commission, Division of Licensing and Regulation, Washington 25, D. C.

### Waste Disposal Licenses Granted

The AEC announced in December 1958 that it proposes to license the Industrial Waste Disposal Corporation, Houston, Texas, to dispose of radioactive waste material into the Gulf of Mexico<sup>7</sup> and in April 1959 that it proposed to renew the licenses of the U. S. Naval Radiological Defense Laboratory<sup>8</sup> and the National Institute of Health<sup>9</sup> to dispose of wastes into the Pacific and Atlantic, respectively.

### References

1. C. E. Guthrie, Radiochemical Processing Costs in an Expanding Nuclear Economy, Paper presented at the 1959 Nuclear Congress, Cleveland, Ohio, April 1959.
2. AEC Sets Base Charges for Uranium-233 and Plutonium Made Available for Research and Development Uses, AEC Press Release A-320, Dec. 3, 1958.
3. AEC Proposes Regulatory Amendments Setting Lower Limits on Radiation Exposures, AEC Press Release B-63, Apr. 23, 1959.
4. *Federal Register*, 3537, Vol. 24, May 2, 1959.
5. *Reactor Fuel Processing*, 2(1): (January 1959).
6. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., Vol. 6, No. 1, January 1959.
7. AEC Proposes to License Houston Firm to Dispose of Low-Level Radioactive Wastes in Gulf of Mexico, AEC Press Release A-323, Dec. 4, 1958.
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## PREPARATION FOR FUEL PROCESSING

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The large number of proposed reactor designs involve an increasingly large number of fuel types. Before actual processing begins, most fuels require storage, mechanical or chemical disassembly of the element, dissolution of the fuel proper, and perhaps a chemical pretreatment prior to processing.

### *Mechanical Processing*

Mechanical removal of the cladding material from fuel elements has several advantages, including smaller aqueous waste volumes, the use of less corrosive reagents for dissolving the fuel material when the difficult-to-dissolve cladding is removed, and increased plant capacity in the absence of dissolved cladding material being added to process streams.

In work at Hanford<sup>1</sup> continued tests with a 40-ton hydraulic shear equipped with a notched ( $\frac{1}{2}$  by  $\frac{3}{4}$ -in. rectangular notches) upper blade and semicircular lower stationary blade, and cutting simulated reactor fuel assemblies (ceramic-filled stainless and copper tubing), both in air and submerged in water, showed:

1. Notched blade performance is inferior to that of either straight or V blades; chopped material catches in the notches.

2. Semicircular stationary blade performance is superior to that of straight or V blades.

3. Water submergence had no effect on the shearing performance. Some fine ceramic was dispersed in the water.

4. A low-velocity water flush through the shear throat reduced accumulation of fines in the throat by about 75 per cent.

"Wet" shearing of reactor fuel elements may be necessary to control dusting. Ethylene glycol is a candidate for shear bath liquid during the chopping of Na-bonded elements since it is cheap, water-soluble, has a high boiling point, and will react slowly with sodium at water dilutions up to 10 per cent.

High speed movies made to determine shear blade speeds and shearing characteristics in the

40-ton unit<sup>2</sup> show that the  $7\frac{1}{2}$ -in. shearing stroke is complete in  $\frac{1}{6}$  sec. Peak blade velocities of approximately 70 in./sec are obtained which require hydraulic oil flow rates of as high as 400 gal/min.

Studies made with the shear equipped with a straight moving blade and a semicircular stationary blade have indicated that the shear forces required are approximately 10 per cent greater than the force required when both stationary and moving blades are straight. Although slightly greater shear forces are required, this straight semicircular combination is considered the best yet tested since the tube bundles are less disturbed (not fanned-out) during shearing. Life testing has begun with this blade combination using 420 stainless-steel blades. By using conditions adjusted to accelerate blade wear, only minor blade wear was noted after approximately 2000 sq in. of steel (and stainless steel) had been cut. At that time the shearing force required had increased approximately 10 per cent.

"Cold-sawing" (multiple milling cutter teeth on a circular blade) is being investigated as an attractive alternate for friction cutting of end fittings from power reactor fuels. Cold-sawing combines the advantages of hacksawing (low cutting speeds and heat generation, larger saw particles) and circular friction sawing (longer blade life, simple equipment, easier remote blade change, maintenance).

At ORNL<sup>3</sup> it was shown that stainless-steel-uranium dioxide core fuel tubes in a typical fuel-element array were chopped into short sections satisfactorily by the use of a 125-ton Manco hydraulic shear with "line of contact" blades.<sup>4</sup> Rapid cutting and flattening of the bundle decreased the degree of closure on the fuel tubes.

In leaching tests on sheared  $\frac{3}{8}$ -in.-diameter stainless-steel-clad-uranium dioxide core fuel sections 1.5 in. long, the sections of tubes were leached free of uranium dioxide by 10M nitric acid in approximately 25 min.<sup>4</sup>

Tests of the use of abrasion disks<sup>5</sup> for sawing stainless-steel rods indicated that at a disk speed

of 10,770 surface feet per minute and a cutting rate of 10 in. per minute, approximately 4500 cuts through a 0.5-in. stainless-steel rod would reduce the diameter of the 10-in. cutting disk by a factor of 2. It was also shown that a stainless-steel-clad porcelain core (stand-in for uranium dioxide) could not be cut successfully with a 24-in. abrasive disk running at 11,000 surface feet per minute.

A 36-tube porcelain-filled stainless-steel tube bundle was sheared into short sections with a 125-ton Manco hydraulic shear with "line of contact" blades. After 65 cuts through the entire bundle, the clearance between the shear blades increased from 2 to 18 mils without changing the efficiency of the shear. In tests with uranium dioxide-filled single tubes about 30 per cent of the uranium dioxide contained in a 0.5-in. tube approximately 1 in. in sheared length was dislodged by the shearing action as dust, 50 per cent of which was less than  $150\mu$  in diameter.

### *Chemical Dejacketing*

An attractive alternate to mechanical dejacketing or complete dissolution of fuel elements is selective chemical dissolution of fuel jackets and structural components. The fuel cores thus exposed can then be dissolved by another reagent in a second step. The principal jacket materials are aluminum, zirconium or Zircaloy, and stainless steel.

### *Removal of Zirconium and Zircaloy Jackets*

Further data on the rate of dissolution of zirconium on Zircaloy-2 in mixtures of nitric and hydrofluoric acid have been obtained at the Idaho Chemical Processing Plant.<sup>6</sup> The effect of the concentration of nitric acid (2M to 13M) on the rate of dissolution of Zircaloy-2 coupons was studied at the reflux temperatures (98 to 115°C). Initial rates of dissolution varied from 30 to 5 mg/(sq cm)(min); average rates over a 2-hr period varied from 2.6 to 5.3 mg/(sq cm)(min).

Studies of reprocessing fuel elements clad with zirconium<sup>7,8</sup> revealed that increasing nitric acid concentration increased the dissolution rate of zirconium in solutions containing less than 1.0M hydrofluoric acid. Nitric acid concentrations above 3M had little or no effect.

For Zircaloy-clad fuel elements having either an oxide core or a uranium-niobium-zirconium alloy core, the Zirflex process, in which 6M ammonium fluoride-1M ammonium nitrate is used as a dissolving agent, is being studied.<sup>1,5</sup>

Zircaloy-2 jackets can be dissolved in 6M ammonium fluoride-1M ammonium nitrate and the exposed uranium dioxide core in 10M nitric acid. The losses of uranium resulting from the dissolution of uranium dioxide in the decladding solution were 0.02 per cent both for unirradiated fuel and for irradiated samples.

Two tentative flow sheets, in which 6M ammonium fluoride is used as the dissolvent, have been developed for the Submarine Thermal Reactor (STR) type fuel<sup>9</sup> (1 per cent uranium, 97 per cent zirconium, and 2 per cent tin). One flow sheet (Fig. 2) resembles that used at ICPP with the exception that the dissolvent is 6M ammonium fluoride rather than hydrofluoric acid. Aluminum nitrate, nitric acid, and chromic acid are added to convert the ammonium fluoride dissolution products to a solution suitable for solvent extraction. Both dissolution and feed preparation can be performed in a single stainless-steel vessel. A principal advantage in this process is that fuels containing greater than 1 per cent uranium can be processed in the present ICPP equipment.

In the second flow sheet (Fig. 3), the ammonium fluoride dissolution products are treated with 7.5M ammonium hydroxide to cause precipitation by hydrous uranium and zirconium oxides. These hydrous oxides are separated from the supernatant solution by filtration or decantation and are dissolved in nitric acid to yield a solvent-extraction feed of low fluoride and increased uranium content. The ammonium fluoride-ammonium hydroxide filtrate is recycled for use as dissolvent.

Ammonia removal from the dissolver system in the Zirflex process has been one of the major difficulties in approaching maximum dissolution rates of Zircaloy.<sup>2</sup> The boil-up rate, air rate, and refluxing condensate temperature all affect the rate of removal of ammonia. Air sparging and water-boil-off have been effective with cold condensate temperatures. By operating with a hot (85°C) condensate reflux, an air rate of 0.4 scfm/sq ft of Zircaloy surface and a calculated boil-up rate of 11.7 lb/(hr)(sq ft) of Zircaloy, dissolution of  $\frac{1}{16}$ -in.-thick oxidized sheets of Zircaloy was complete in 2.7 hr. This rate exceeded those obtainable with cold condensate and approached the best values obtained under laboratory conditions.

## REACTOR FUEL PROCESSING

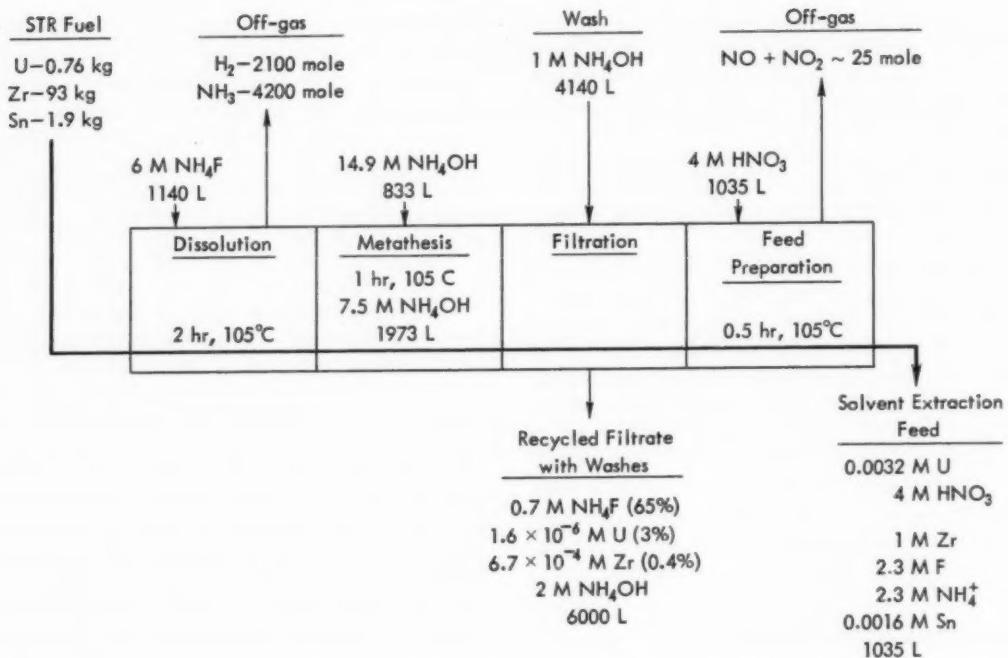


Figure 2—Tentative flow sheet for aqueous fluoride dissolution of STR type fuel by a modified Zirflex process with fluoride recycle.<sup>9</sup>

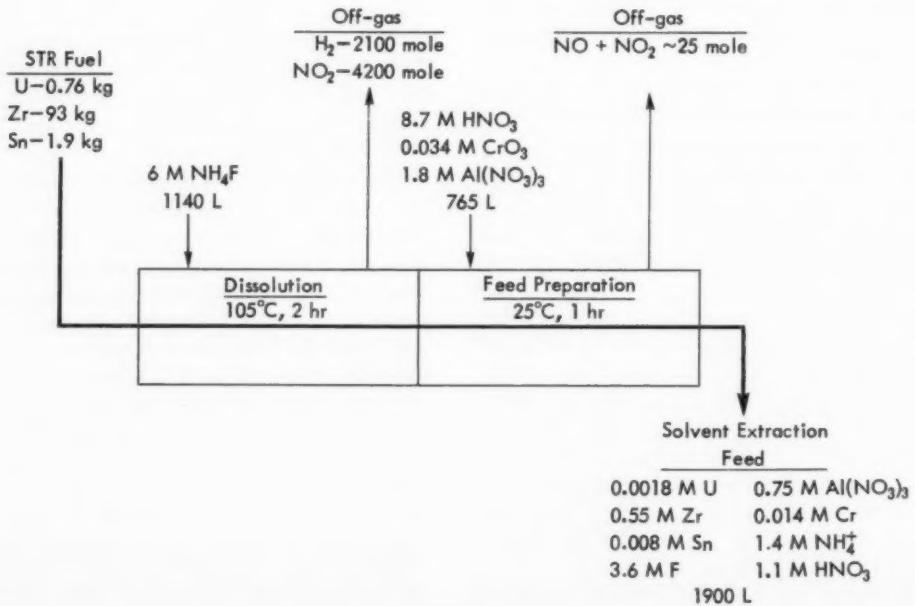


Figure 3—Tentative flow sheet for aqueous fluoride dissolution of STR type fuel by a modified Zirflex process.<sup>9</sup>

### Removal of Stainless-steel Jackets

A Sulfex flow sheet for Yankee Atomic Power Reactor (YAPR) fuel was presented in an earlier Review.<sup>10</sup> Recent modifications of this flow sheet provide for the dissolution of the cladding in 200 per cent excess of boiling 4M sulfuric acid; the spent decladding solution is sent to waste disposal. Dissolution of the exposed uranium dioxide core with 8M nitric acid provides, after suitable adjustment, a feed solution for subsequent processing by solvent extraction.<sup>11</sup> With unirradiated fuel specimens, dissolution of type 304L stainless-steel cladding proceeded at rates of 2 to 5 mg/(sq cm)(min) in boiling 4M sulfuric acid; the rate appeared somewhat lower with irradiated specimens. From 0.01 to 0.02 per cent of the uranium was lost to the decladding solution.

Stainless-steel cladding which had been exposed to steam at 1200 psig and to oxygen at 800 psig did not react with boiling 6M sulfuric acid until it was activated by contact with unoxidized stainless steel.<sup>4</sup> After the reaction started, the stainless-steel cladding dissolved at a rate of 15 to 20 mg/(sq cm)(min).

Stainless steel was dissolved satisfactorily by electrolysis in nitric acid.<sup>8</sup> The rate of dissolution for both a-c and d-c varied linearly with current density; variations in acidity, salt concentration, and temperature had little or no effect over wide ranges.

### Dissolution

#### Simultaneous Dissolution of Jacket and Core

1. *Zirconium Fuel Elements.* Zirconium-containing fuel elements may be dissolved by the use of aqueous fluoride-nitric mixtures or by hydrochlorination (Zircex process). Codissolution of cladding and core material of a reactor fuel material consisting of a zirconium-clad alloy containing 90 wt.% uranium and 10 wt.% molybdenum is being examined at Savannah River.<sup>8</sup> The data indicate that fuel elements of this type can be dissolved in boiling nitric acid-hydrofluoric acid mixtures practically and without excessive corrosion in a dissolver made of wrought 309 Nb stainless steel.

Work continues on the Zircex process (reported in previous Reviews<sup>10,12-14</sup>) at ORNL.<sup>15</sup> The Zircex process is a chemical method for separating zirconium and uranium by reacting

spent fuels with anhydrous hydrogen chloride at 500°C, producing volatile zirconium tetrachloride and a nonvolatile uranium-containing residue. Reaction times for the hydrochlorination step for fully enriched-fuel assemblies would probably be less than 10 hr and for decladding uranium dioxide-containing fuels less than 3 hr. For the thick-plate Experimental Boiling Water Reactor (EBWR) fuel assemblies, reaction times of 30 hr or more would probably be required.

At present, 11 reactors use zirconium as the primary structural or cladding material. The fuels for these reactors can be grouped into three types: (1) fully enriched fuels containing less than 10 per cent uranium; (2) ceramic fuels of uranium dioxide pellets or platelets clad in Zircaloy-2; and (3) niobium-containing fuels. Some of these reactors and their fuels are summarized in Table II-1.

Flow diagrams showing possible processing schemes for each of the fuel types are presented in Figs. 4, 5, and 6. For all three, the zirconium reacts to form volatile zirconium chloride, which passes out of the hydrochlorination vessel to a condenser. Any tin in the fuel is also vaporized, and the mixture of zirconium and stannous chlorides is stored as a solid. Fission products are scrubbed from the hydrogen, which can be burned with chlorine to form hydrochloric acid for recycle or burned to water for disposal.

2. *Stainless-steel Fuel Elements.* Methods of dissolution of fuel elements containing stainless steel include dissolution in nitric acid-hydrofluoric acid mixtures (Niflex), in dilute aqua regia (Darex), and in dilute sulfuric acid (Sulfex).

A Hastelloy F dissolver system for the Niflex process has been installed at Hanford. Preparatory to carrying out a Niflex dissolution on irradiated uranium metal, acid consumption studies were conducted with unirradiated uranium.<sup>16</sup> Acid consumptions on 304L stainless steel in 1M nitric acid, 2M hydrofluoric acid, and in 3M nitric acid, 2M hydrofluoric acid were, respectively, 3.7 and 3.1 moles acid consumed per mole of stainless steel dissolved.

The first Niflex dissolution of 304L stainless steel gave a terminal stainless-steel concentration of 12.7 g/liter after four hours of operation with a 1M nitric acid-1M NH<sub>4</sub>HF<sub>2</sub> solution.<sup>2</sup> Addition of more nitric acid was necessary before any further dissolution would occur to approach the normal laboratory saturation of some 22 g/liter. Equipment operation was ex-

Table II-1 ZIRCONIUM-CONTAINING REACTOR FUELS<sup>15</sup>  
(September 1958)

Reactor	Fuel composition	Clad material	Element configuration
<i>Premium Power Fuels</i>			
Pressurized Water Reactor Core-1	6.33% U-93.67% Zircaloy-2*	Zircaloy-2	Plate
Pressurized Water Reactor Core-2	9.7% U-90.3% Zr	Zircaloy-2	Plate
<i>UO<sub>2</sub>-containing Fuels</i>			
Pressurized Water Reactor Blanket-1	UO <sub>2</sub> pellets	Zircaloy-2	Tube
Pressurized Water Reactor Blanket-2	UO <sub>2</sub> platelets	Zircaloy-2	Plate
Commonwealth Edison	UO <sub>2</sub> pellets	Zircaloy-2	Tube
<i>Niobium-containing Fuels</i>			
Experimental Boiling Water Reactor	93.5% U-5% Zr-1.5% Nb	Zircaloy-2	Plate

\*The composition of Zircaloy-2 is 1.25-1.65% Sn, and the remainder is zirconium with traces of Fe, Cr, and Ni.

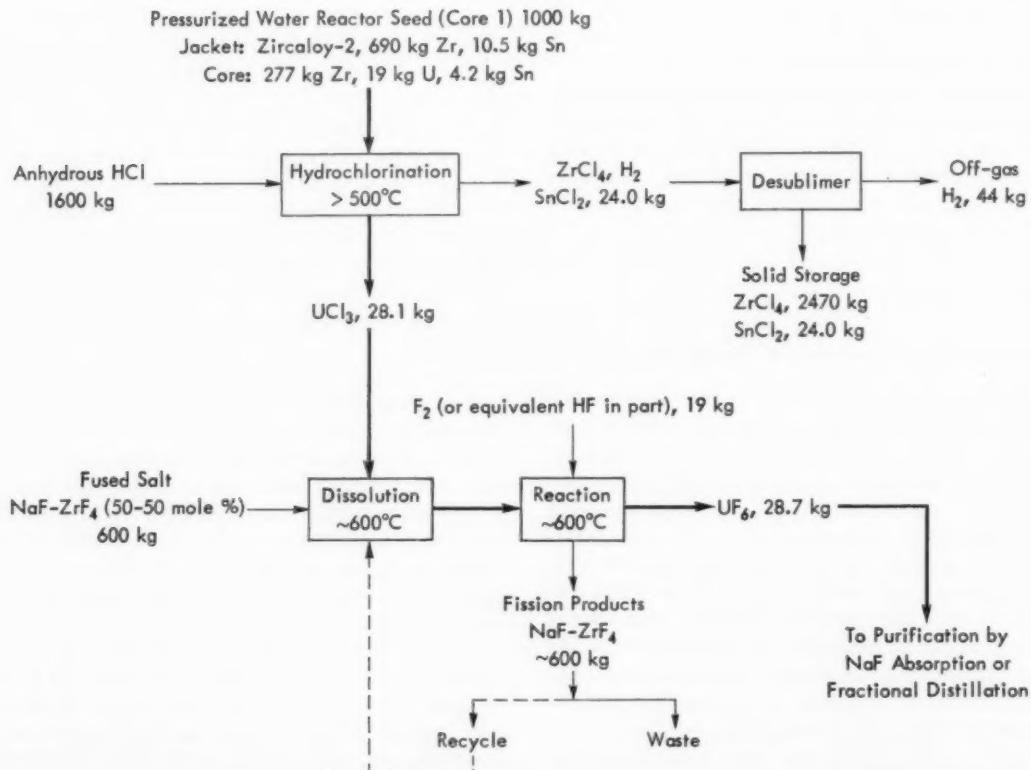


Figure 4—Zircex process for hydrochlorination of fully enriched fuels with purification by the fluoride volatility process.<sup>16</sup>

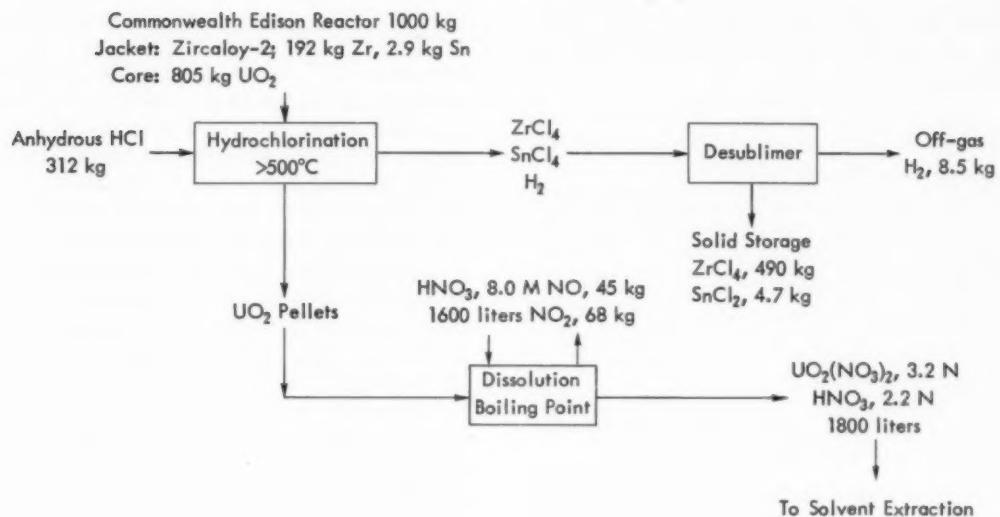


Figure 5—Zircex process for hydrochlorination of normal or slightly enriched uranium dioxide-containing fuels with purification by solvent extraction.<sup>15</sup>

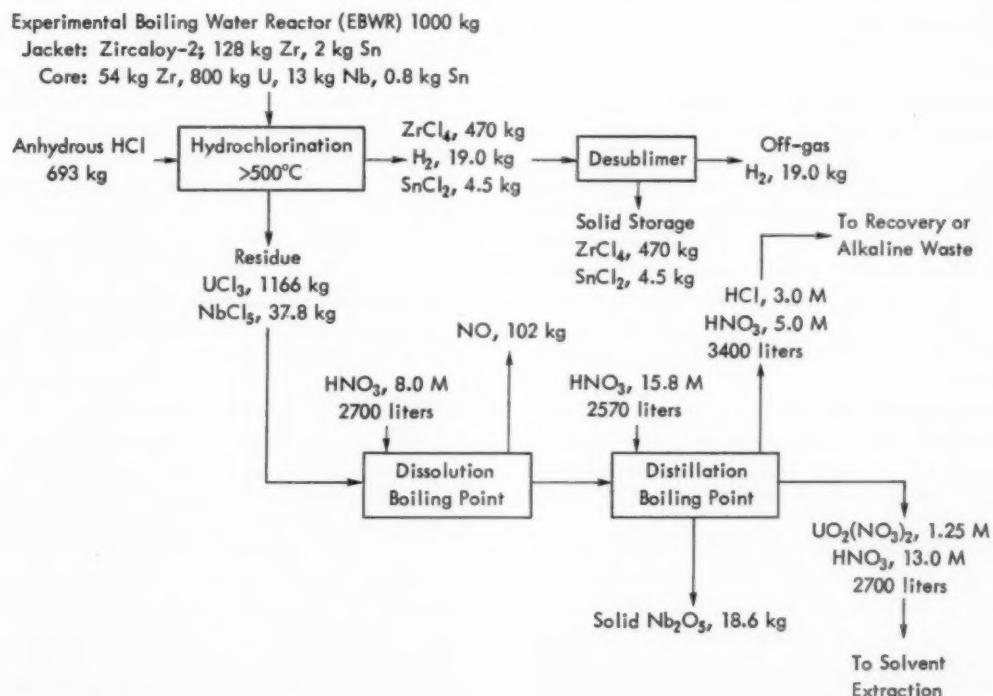


Figure 6—Zircex process for hydrochlorination of EBWR fuel with purification by solvent extraction.<sup>15</sup>

cellent. Six additional runs<sup>17</sup> with 2M nitric acid-1M NH<sub>4</sub>HF<sub>2</sub> solutions led to the following observations:

1. The terminal solutions consistently contained 23 to 26 g of stainless steel per liter after four hours of operation.
2. The charge was at least 85 per cent dissolved after one hour of boiling with a fluorine-to-stainless-steel mole ratio of 5.
3. Off-gas analysis after one hour of dissolution averaged 1 per cent oxides of nitrogen and 1 per cent hydrogen with an air flow of 0.34 scfm/(sq ft of stainless-steel surface).
4. Dissolution was 91 to 99 per cent complete after four hours of boiling with a fluoride-to-stainless-steel mole charge ratio of 5.

Studies of the Darex process have been made at ORNL<sup>5,9,18,19</sup> and HAPO.<sup>1,2,16</sup> In a single continuous dissolution run,<sup>19</sup> made in a 6-in. glass dissolver with a downdraft condenser, a prototype stainless-steel APPR fuel element weighing 5.46 kg was dissolved in 15 min using 2M hydrochloric acid-5M nitric acid feed. A dissolver product loading of 87 g/liter was produced at a dissolvent feed rate of 4.5 liters/min. The apparent dissolution rate based on the initial surface area of the element was 18 mg/(sq cm) (min).

In additional chloride removal tests<sup>9</sup> on a continuous 60 per cent nitric acid addition procedure of the batch Darex process, chloride content of solvent-extraction feed ranged from 130 ppm to as high as 3195 ppm, rather than the less than 50 ppm value obtained in the first tests. Recovery of 13.2M nitric acid is apparently not possible because of loss of dissolved N<sub>2</sub>O<sub>3</sub> gas from the recovered acid during refluxing to remove traces of chloride prior to recycle.

In continuous dissolution tests with unirradiated APPR fuel,<sup>5</sup> uniform dissolution rates of 275 g of fuel element per minute were obtained with a constant rate of addition of mixed acid of 4.5 liters/min.

Three full-size unirradiated sintered uranium dioxide-stainless-steel (APPR) elements dissolved in 2M hydrochloric acid-5M nitric acid in 1 hr except for the braze metal.<sup>3</sup> The average rate was 28 g/min at a dissolvent rate of 4.3 liters/min.

A sequential dissolution of 304 stainless-steel pipe and annular pieces of sintered uranium

dioxide was performed in a pilot unit.<sup>1</sup> Continuous addition of 3.75M hydrochloric acid and 4.7M nitric acid developed a cyclic and unstable reaction with stainless steel at a flow rate less than about 0.01 gal/min/sq ft of stainless-steel surface. At higher rates the reaction proceeded smoothly. Dissolution of the uranium dioxide proceeded at rates of 100 mils/hr in 2.6M chloride, 3M acid, and 1.2M stainless steel.

One method of preparing a solvent-extraction feed from fuel elements jacketed in stainless steel consists of complete dissolution in aqua regia, 5M nitric acid-2M hydrochloric acid. Three series of experimental runs were carried out in titanium pilot plant equipment in an effort to define the variables associated with this process.<sup>16</sup> In the first series, it was shown that nitrate-to-chloride mole ratios of less than 4 give a dissolution rate of dejacketed stainless-steel slugs of 180 mils/hr for solid 8-in. uranium slugs. In the second series of runs, it was demonstrated that controlling the rate of stainless-steel dissolution by slowly metering 4.6M nitric acid-1.8M hydrochloric acid into the dissolver was feasible. The third series of experiments was directed toward the dissolution of stainless steel and uranium dioxide. Type 304 stainless-steel tubing having a 32-mil wall thickness (one piece wrapped with a small piece of copper wire to preclude passivation) was dissolved smoothly and completely in 1.25M hydrochloric acid and 2M nitric acid in 2 to 3 hr.

One hundred pounds of stainless-steel-clad uranium dioxide rods were dissolved in the Darex pilot plant unit by the metered addition of 3M hydrochloric acid, 4M nitric acid.<sup>2</sup> The procedure used permitted an approximate determination of the heat of dissolution for stainless steel. The measured value of 2700 Btu/lb agrees fairly well with the 2300 Btu/lb figure calculated from thermodynamic data.

A series of chloride removal runs was made in the Darex pilot plant unit<sup>16</sup> on solutions containing uranium and stainless steel. Pertinent findings are: (1) the continuous addition of nitric acid through a submerged feed point offered no advantage over a top feed point; (2) a greater difficulty in removing chloride from a solution high in stainless-steel content was again demonstrated with both concentrated and dilute Darex solutions; and (3) the addition of water through a submerged feed point for nitric acid removal is superior to a top feed point.

**3. Aluminum Fuel Elements.** Present and proposed fuels for nuclear reactors include uranium-aluminum alloys. Several scouting studies have been conducted<sup>1</sup> to determine typical dissolution rates of  $\frac{1}{2}$ -in.-diameter uranium-aluminum alloys in mercuric nitrate acid mixtures. Essentially complete dissolution of the 0.9 to 2.25 per cent uranium alloy was achieved in 1 to 2 hr using boiling 3M to 8M nitric acid with 0.01M mercuric nitrate as a dissolution agent at charge mole ratios of about 4 nitric acid to 1 aluminum. The initial concentrations of 5M and 8M nitric acid resulted in self-sustained boiling, potential foaming problems, and required cooling of the dissolver to maintain control. The dissolution rates secured with 3M nitric acid were adequate (approximately 150 mils/hr), and very little external heat was required to maintain boiling conditions.

Other studies of this type are reported by Evans<sup>20</sup> which confirm the feasibility of continuously dissolving aluminum-jacketed uranium slugs in mercury-catalyzed nitric acid. A number of experiments have been reported at ICPP on dissolution of aluminum and aluminum alloys.<sup>6,21,22</sup> General relationships for the performance of a continuous flooded dissolver, derived in an earlier report,<sup>21</sup> were applied to available pilot plant data on the mercury-catalyzed dissolution of 2S aluminum in nitric acid.<sup>22</sup> The relationships were based on nonmixing flow of the liquid phase, uniform metal packing characteristics, and a first order reaction rate law. The dissolver was a 2-in. Pyrex column, and the effective height ranged from 8 to 10 ft. Some data were available also for the dissolution of elements in which the height of the bed of elements varied from about 1 to 10 ft.

The average nitric acid concentration in the dissolvent feed was 5.6M. Effective reaction velocity constants were obtained for catalyst concentrations ranging from  $1.5 \times 10^{-6}$  to  $3.75 \times 10^{-4}$  M Hg<sup>++</sup>.

The general equation was used to predict the effect of the shape of metal elements, the flow rate of the dissolvent, and the height of bed of elements on the dissolution rate. The calculated rate followed the trends in the data and showed the model as expressed by the dissolver equation to give a picture generally consistent with experimental results from the pilot plant. Straughn and Tarpley<sup>23</sup> have investigated the ultrasonic accelerated dissolution of the high-

temperature and corrosion resistance metal alloys nichrome, Inconel X, and Kanthal.

#### Dissolution of Dejacketed Material

When fuel jackets can be removed mechanically or chemically or the fuel sheared into pieces, dissolution of the core becomes a separate and probably simpler feed preparation approach.

Studies of uranium and uranium dioxide dissolution have been made at Hanford.<sup>17</sup> Dissolution rates for ingot uranium and sintered uranium dioxide in proposed core dissolvent solutions (nitric acid-hydrofluoric acid-aluminum nitrate) were determined. The tests were made in boiling solutions; constituent concentration range studies were nitric acid from acid deficient to 3M, hydrofluoric acid from 0.1M to 1.0M, aluminum nitrate from 0M to 1.0M, and uranyl nitrate from 0M to 0.6M. Dissolution rates for ingot uranium were in the range from 1 to 5 g/(sq cm)(hr) in the absence of aluminum or in the presence of aluminum if the aluminum-to-fluorine mole ratio was less than 1. At an aluminum-to-fluorine mole ratio of 1 the dissolution rates ranged from 0.2 to 0.5 g/(sq cm)(hr). Dissolution rates for sintered uranium dioxide were appreciably less than those for metallic uranium. They ranged from 0.1 to about 1 g/(sq cm)(hr). Addition of ferric nitrate to the dissolvents increased the dissolution rate appreciably.

Dissolution rates of sintered uranium dioxide fuel cores were determined under a variety of conditions.<sup>1</sup> Typical rates secured are as follows:

Solution composition					Rate, mils/hr
NO <sub>3</sub>	HNO <sub>3</sub>	UNH	ANN		
10.6	10.0	0.0	0.2	110 to 160	
6.9	2.7	1.8	0.2	13 to 20	
6.9	0.9	2.7	0.2	2 to 6	

Exposure of uranium dioxide irradiated to about 460 Mwd/ton and cooled nine months to boiling 4M sulfuric acid resulted in dissolution of the uranium dioxide at a constant rate of 0.02 per cent per hour.<sup>2</sup> Recent studies<sup>1</sup> of the rate of dissolution of irradiated uranium dioxide (irradiated to 500 g plutonium per ton uranium and cooled about 20 months) in boiling 4M sulfuric acid indicate dissolution rates of  $1 \times 10^{-4}$  g/(hr)(sq cm) and  $7 \times 10^{-5}$  g/(hr)(sq cm) for ura-

nium and plutonium, respectively, corresponding to a reaction rate of about 0.05 per cent per hour. These rates were lower by a factor of 10 when stainless steel was being simultaneously dissolved at a rate of 0.1M per hour. Surprisingly, the rate of dissolution of unirradiated uranium dioxide was found to be depressed by a factor of 10 also in the presence of dissolving stainless steel.

The dissolution of uranium-molybdenum alloys has been investigated at Hanford. When uranium-3 per cent molybdenum alloy is dissolved (or disintegrated) in boiling nitric acid, large amounts of finely divided yellow-white solids are formed; dissolution of this alloy in boiling nitric acid-ammonium fluoride-aluminum nitrate solutions, without leaving appreciable solids, is readily accomplished if the aluminum to fluoride mole ratio is 0.5 or less, the fluorine to molybdenum (terminal) mole ratio is about 30, terminal uranium concentration is about 0.4M, and terminal acidity is about 1M.<sup>1,2,17</sup> Instantaneous dissolution rates, under these conditions, are >1 g/(sq cm)(hr) and appear adequately high. The solids formed in the dissolution of uranium-3.0 wt.% molybdenum alloy by nitric acid contain about 6 per cent of the uranium. Metathesis of these solids with sodium hydroxide is readily accomplished with small (<0.1 per cent) loss of uranium to the supernatant liquid.<sup>3</sup> The metathesis residue is readily soluble in nitric acid.

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## RESEARCH AND DEVELOPMENT ON FUEL PROCESSING

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### Solvent Extraction

#### Modifications of Redox and Purex Processes

Currently, production facilities employ either the Redox or Purex solvent-extraction processes for the recovery of uranium and plutonium. The Redox extractant is methyl isobutyl ketone; that for Purex is tributyl phosphate (TBP). A continuing program attempts to improve these processes and to adapt them to nonproduction reactor fuels.

The throughput in Purex plants is frequently limited by the capacity of the uranium stripping (1C) column. In the 1C column the uranium-bearing solvent is contacted with water or very dilute acid. These conditions favor the formation of slowly coalescing emulsions; hence, flooding often occurs at relatively low throughput. Methods of increasing the capacity of the Purex 1C columns without modification of column intervals have been reported.<sup>1</sup> Of the variables studied (interface position, pulse amplitude, and aqueous-to-organic flow ratio) only the interface position gave promise of improved capacity. Location of the interface at the bottom (rather than the normal top position) increased maximum stable column flooding capacity by a factor of 1.4 to 2.0. The change in stripping efficiency, if any, was not reported. Since bottom interface operation makes the organic phase continuous, some penalty in extraction efficiency would not be surprising.

Improvements in the Purex type Thorex process for the decontamination and separation of U<sup>233</sup> and thorium were obtained by a head-end treatment with diisobutylcarbinol (DIBC) prior to TBP extraction.<sup>2</sup> Protactinium is not extracted by TBP; therefore fuel storage for as long as nine months is required to permit the decay of protactinium to U<sup>233</sup>. By recovering the protactinium in a head-end step the volume of radioactive waste to be stored can be reduced by as much as 95 per cent. In tracer-level runs 99 per cent of the protactinium was recovered from feed solutions (1M thorium nitrate, 0.6M

aluminum nitrate, 4M nitric acid) with DIBC and decontamination factors obtained as follows: uranium, 600; thorium, 60,000; ruthenium, 5000; zirconium-niobium, 250; rare earths, 4000. Studies of radiation damage to DIBC showed no impairment of extraction ability at dosages as high as 105 watt-hr/liter.

Details of the recovery of multigram quantities of neptunium from diffusion plant fluorination ash by the "Nethix-1" process are available.<sup>3</sup> This process provides a neptunium product with less than 1 ppm thorium or uranium. A key step in the process is the stabilization of Np(V) in 1M nitric acid with hydrogen peroxide. Neptunium was separated from thorium with a decontamination factor of 20 by solvent extraction with 5 per cent TBP. Thorium and neptunium were further separated in a chloride system and uranium was removed in a nitrate system with 30 per cent TBP. The over-all process requires a series of operations involving solvent extraction, ion exchange, and evaporation.

For recovery of neptunium in the Purex first cycle, favorable conditions are high acid, high nitrate, high temperature, and low aqueous phase nitrous acid concentration. Nitrous acid is objectionable because it reduces the TBP extractable Np(VI) to the inextractable Np(V).<sup>4</sup>

Testing continues of modified Purex and Redox processes for nonproduction reactor fuels. A satisfactory procedure for the recovery of uranium and plutonium from Detroit Edison core elements (90 per cent uranium, 10 per cent molybdenum with zirconium cladding) was demonstrated.<sup>5</sup> The fuel elements were dissolved by means of the Niflex process (0.1M hydrofluoric acid-3.0M nitric acid). Aluminum nitrate to give 0.4M in the feed was added to the dissolver solution to prevent excessive plutonium losses in subsequent solvent extraction. Preliminary data had shown the aqueous phase nitrate concentration to be the principal factor controlling the plutonium losses. Extraction of uranium and plutonium in a miniature mixer-settler with 10 per cent TBP was satisfactorily accomplished with plutonium losses of less than 0.5 per cent.

For the processing of aluminum-base fuel, TBP extraction from dibasic solution provides a promising separations scheme.<sup>6</sup> Diban (dibasic aluminum nitrate— $\text{Al(OH)}_2\text{NO}_3$ ) is produced by hydrolysis of aluminum in aluminum nitrate systems. Diban is also referred to as acid-deficient aluminum nitrate in that



Extraction coefficients are presented in Fig. 7 for the distribution of tracer uranyl nitrate between diban solution and 5 per cent TBP.

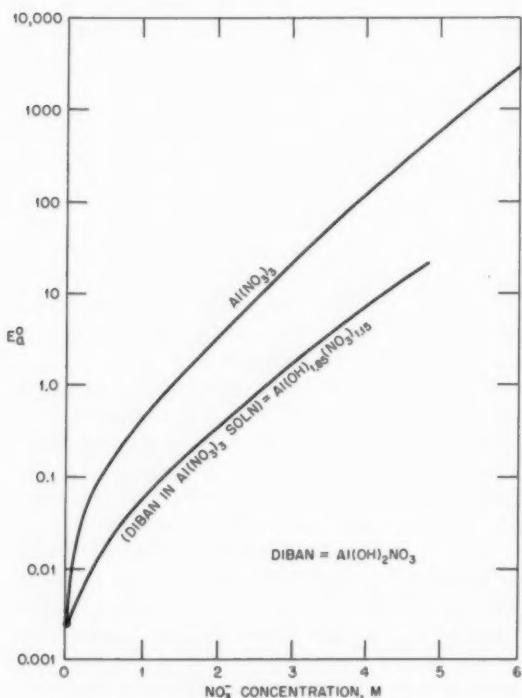


Figure 7—Distribution of tracer uranium between diban solution and 5 per cent tributyl phosphate.<sup>6</sup>

Employing Darex feeds (stainless-steel fuels dissolved in 5M nitric acid-2M hydrochloric acid), batch tests of a low-acid Redox process showed indications of poor beta-gamma decontamination. Tests of Redox processing of Niflex feed (stainless-steel fuels dissolved in 1M nitric acid-2M hydrofluoric acid) showed over-all decontamination factors 30-fold lower than standard Redox conditions.<sup>63</sup>

### Development of Alternate Solvents

Currently under development are a number of solvent-extraction processes based on various organonitrogen and organophosphorus extractants. These new extractants have been found to be adaptable to a wide variety of separations problems.

Di(2-ethylhexyl) phosphoric acid (D2EHPA) extracts strontium from neutralized aqueous radioactive waste;<sup>7</sup> the extraction coefficient,  $E_d^0$ , is 200 between 0.1M sodium D2EHPA in Amsco and a 0.5M sodium nitrate solution at a pH of 5.

At low uranium concentrations extraction coefficients for acid organophosphorus reagent vary directly as the square of the organic phase acidity. Extraction coefficients for polyvalent cations with dialkyl phosphates are much greater than those obtained with neutral reagents such as TBP. An interesting phenomenon is that the addition of small amounts of a neutral reagent to an acidic dialkyl phosphate results in extraction coefficients considerably in excess of those obtained with either of the pure reagents. One suggested explanation for this synergistic enhancement of extraction coefficient is based on the following thermodynamic postulate:<sup>8</sup> Acid reagents are dimeric in kerosene diluent. To form a monomeric cation addition compound, the dimeric structure must be broken. The addition of a mole of monomeric neutral reagent eliminates the need for monomerizing a mole of the dimer. The net difference in free energy between the two systems, roughly estimated as 8 kcal/mole, could account for some of the partition coefficient enhancement.

A more detailed study of the remarkable synergistic effect noted with certain combinations of dialkylphosphoric acids and neutral organophosphorus compounds is available.<sup>9</sup> Experimental data were obtained in a large number of batch tests, and synergistic effects of as much as two orders of magnitude were noted (see Fig. 8). These effects were observed in nitrate, chloride, sulfate, and phosphate systems. Elements showing a synergistic enhancement of extraction coefficients were Pu(IV), Pu(VI), and U(VI). Uranium(VI), V(IV), aluminum, and molybdenum showed little effect. For both the acidic reagent and synergistic mixture, addition reactions with the acidic dimer were proposed: with acidic reagent only

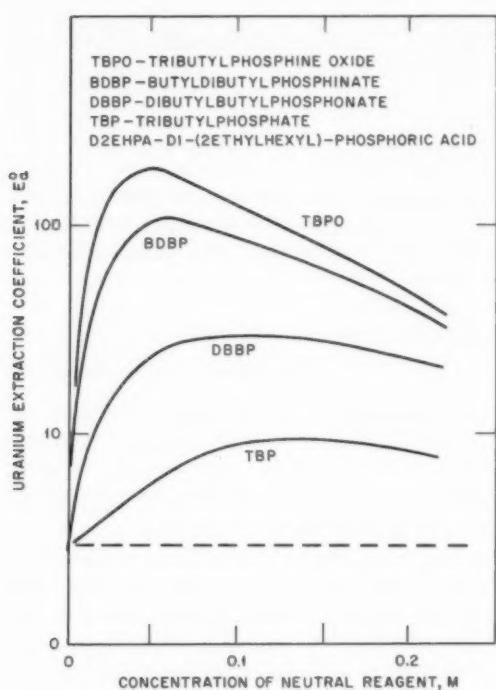
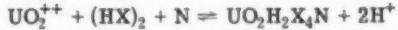


Figure 8—Synergistic effect of neutral reagents. Organic phase, 0.1M D2EHPA in kerosene diluent plus neutral reagent. Aqueous phase, 1.5M H<sub>2</sub>SO<sub>4</sub> initially 0.004M U(VI).<sup>9</sup>



with synergistic mixture containing neutral reagent, N



Values of thermodynamic functions for the extraction of uranyl nitrate and nitric acid with dialkyl phosphonates were estimated from the variation of extraction coefficients over the temperature range 0 to 50°C.<sup>10</sup> Data were obtained for 21 compounds of the type



Values of  $\Delta S$  suggest that an open structure is retained by the extracted molecules. It appeared that the bond formed with the uranyl nitrate ion is substantially altered as substituents on the phosphorus atom are replaced by various radicals.

Other data available which compare the extractive power of a number of neutral organophosphorus compounds show that addition compounds (dissolvates) are formed in most cases.<sup>11</sup> In general, electronegative substituents decrease the extraction coefficients. For tributyl extractants, the relative decreasing order of extraction power was phosphine oxide, phosphinate, phosphonate, and phosphate. Data for a number of neutral reagents are presented in Table III-1.

Table III-1 COMPARATIVE EXTRACTION COEFFICIENTS FOR NEUTRAL<sup>11</sup> ORGANOPHOSPHORUS REAGENTS

Extractant: 0.19M in benzene diluent  
Raffinate: 0.5M nitric acid

Neutral organophosphorus reagent	Partition coefficient, E° <sub>a</sub>	Solvent-to-uranium mole ratio in sat'd. extractant
Tributyl phosphine oxide	380	2:1
Butyldibutyl phosphinate	120	2:1
Dibutylbutyl phosphonate	10.0	2:1
Tetrabutyl ethylene diphosphonate	5.7	1:1
Tetrabutyl methylene diphosphonate	1.0	1:1
Tri-sec-butyl phosphate	0.54	2:1
Tributyl phosphate (TBP)	0.25	2:1
Triisobutyl phosphate	0.25	2:1
Dibutylalkyl phosphate	0.14	2:1
Dibutyl hydrogen phosphonate	0.12	2:1
Dialkylbutyl phosphate	0.032	2:1
Triakyl phosphate	0.018	2:1
Dibutylphenyl phosphate	0.0035	2:1
Tetrabutyl pyrophosphate	0.001	1:1
Triphenyl phosphate	0.00067	~22:1

#### Solvent Degradation

Process solvents undergo degradation by chemical action and radiolysis. The problems created by radiation damage have become increasingly more critical with the advent of high burn-up power reactor fuels. Thus, current efforts are primarily directed toward assessing

the radiation resistance of various extractants and diluents.

Nitrous acid, which is produced by radiolysis in nitric acid solutions, must be maintained at very low concentrations in Purex systems if neptunium is to be recovered. Some data have been obtained on the rate of nitrous acid formed in Purex scrub solutions.<sup>12</sup> Exposure of scrub solution to a Co<sup>60</sup> source at a dose rate of 0.7 watt-hr/liter gave a nitrous acid formation rate of  $4 \times 10^{-6}$  mole/(liter)(min). An equilibrium concentration of  $3.8 \times 10^{-3}$  mole/liter was reached in 24 hr at 25°C. This equilibrium concentration was relatively insensitive to nitric acid or uranyl nitrate concentration.

New data for radiation degradation of TBP are available.<sup>13</sup> The radiation source, irradiated uranium slugs, was probably more representative of plant conditions than the more popular Co<sup>60</sup> source. The G value (moles formed per 100 ev of energy absorbed) for DBP was 4.5. The variation of DBP yield with sample purity was only 15 per cent.

Some interest has developed in a bauxite slurry treatment for used Purex solvent.<sup>14</sup> A bauxite treatment demonstrated effective removal of several known uranium complexing agents. It also removed emulsifying agents as evidenced by the more rapid coalescence of the treated solvent. However, in the preliminary tests solvent losses, 5 to 8.6 per cent, were prohibitively high.

Feeds prepared from fuel elements containing silica as a thermal bond have presented problems in solvent extraction. The hydrated silica is thought to be the source of an objectionable organophilic carrier involved in the transporting of fission products into the organic phase.<sup>15</sup> On scrubbing of the organic extract the fission products are slowly desorbed and, hence, are only partially removed from the solvent. The retained activity is about 10 per cent zirconium and 90 per cent niobium. A head-end treatment of the feed involving precipitation of macro amounts of Nb<sub>2</sub>O<sub>5</sub> reduced the extraction of these activities into 30 per cent TBP in dodecane by a factor of 50. Tantalum was as effective as niobium.

Studies of radiation damage to the new solvents, organophosphorus and organonitrogen compounds, continue. Dibutyl phosphoric acid (DBPA) and D2EHPA irradiated to 300 watt-hr/liter gave G values, respectively, of 1.6 and 0.7 for dibasic acid, and 0.5 for phosphoric acid.<sup>16</sup>

Three amines, triisooctylamine, Primene JM-T, and alamine, irradiated to 400 watt-hr/liter gave G values of 3.9, 2.9, and 3.1, respectively.

### *Ion-exchange Processes*

Purification and recovery of plutonium and neptunium and separation of binary mixtures of metals have been accomplished by ion-exchange processes.

#### Anion-exchange Process

##### for Purification of Plutonium

The purification of plutonium by absorption from nitric acid has been described in previous Reviews.<sup>17-20</sup> Studies at Hanford<sup>12,21</sup> using Dowex-1 resin have measured plutonium loading and elution kinetics.

During operation of a continuous Purex anion-exchange contactor<sup>12</sup> it was found that the "push time" for the resin increased considerably between the 110th and 140th day of operation. The 140-day resin showed no more broken beads than the 110-day resin and was completely free of the extremely fine material present in both 60-day and 110-day samples. The absence of broken beads and a change in color noted are probably indicative of softening of the resin beads by combined chemical and radiation attack and may explain the increased push times.

Purification of plutonium nitrate solutions by anion exchange is being studied at Hanford. Questions regarding the fission product analyses of anion-exchange experiments for the purification of 1BP plutonium have been resolved now and the results of the earlier experiments can be summarized. With nitric acid alone as the wash solution a zirconium-niobium decontamination factor of slightly greater than  $10^3$  was observed and for ruthenium approximately  $10^4$ . Adding 0.1M phosphoric acid to the wash did not improve the decontamination factor. The addition of low concentrations (0.005M to 0.05M) of hydrofluoric acid to the nitric acid wash improved the separation greatly, giving a zirconium-niobium decontamination factor of approximately  $10^6$ .

Recent Hanford results<sup>4</sup> indicate the efficiency of removal of fission products in the wash cycle decreases as the feed rate of the wash solution is increased. For example, identical volumes of

7.2M nitric acid, 0.01M hydrofluoric acid wash produced zirconium-niobium decontamination factors of  $1.6 \times 10^5$ ,  $2.4 \times 10^4$ , and  $1.8 \times 10^4$  when they were fed at rates of 5.4, 10.1, and 14.8 ml/(min)(sq cm), respectively. Similarly, more efficient removal of fission products can be obtained by increasing the fluoride concentration in the wash solution. The gain in fission-product decontamination is somewhat offset by the greater elution of plutonium which occurs with a high fluoride wash. Use of a high fluoride wash would therefore require that the loading cycle be terminated at a lower average plutonium loading or that a "tailings" column be provided to recover plutonium from the wash cycle effluent.

The chemical feasibility of processing slag and crucible feed, Recuplex,<sup>22</sup> by anion exchange was demonstrated at Hanford<sup>21</sup> in a test run with a laboratory-scale Permutit SK (20- to 50-mesh) column at 60°C. At a flow rate of 10 mg of plutonium/(min)(sq cm) average column loadings were, respectively, 35, 45, and 54 g of plutonium per liter of resin bed at breakthroughs of 0.1, 1, and 10 per cent, respectively.

The efficiency of various resins for removing plutonium from Hanford Recuplex waste was determined by equilibrium measurements at 60°C and compared with the efficiency measured at 28°C. The decreasing order of efficiency for the resins tested at both temperatures was found to be: Dowex-1 (X-4), Amberlite IRA-400 and 401, and Permutit SK. In every case the higher temperature resulted in a more rapid attainment of equilibrium and a lower equilibrium distribution ratio than that found at the lower temperature. An Amberlite IRA-400 column flowing at 0.5 ml/(sq cm)(min) received about 775 column volumes of this waste before reaching a 5 per cent breakthrough. At 11 ml/(sq cm)(min) a 5 per cent breakthrough was reached in about 40 column volumes. At similar flow rates, columns of Permutit SK, IRA-401, and Dowex-1 (X-4) resin required 7, 44, and 245 column volumes, respectively, to achieve a 5 per cent breakthrough. Batch elution experiments performed with these resins indicated the following ranking of the resins in decreasing order of relative speed of desorption: Permutit SK, Dowex-1 (X-4), Amberlite IRA-401 and IRA-400. An over-all evaluation of the resins tested on the basis of presently available data would indicate Dowex-1 (X-4) to be the most

suitable for recovery of plutonium from these wastes.

### Purification of Neptunium

Work carried out at Hanford<sup>12</sup> on purification of neptunium by anion exchange indicates that adequate purification of the Purex neptunium product from all contaminants can very probably be obtained in a single cycle of anion exchange. Adequate plutonium decontamination can be obtained by loading neptunium at room temperature out of 6M nitric acid, 0.1M ferrous sulfamate, 0.1M semicarbazide, and washing at room temperature with 20 column volumes or more of the same solution. This gives poor fission-product decontamination, but it has been shown that applying a second room temperature wash cycle employing 15 column volumes of 8M nitric acid, 0.1M hydrofluoric acid, 0.05M semicarbazide, followed by a 4-column-volume wash employing 8M nitric acid to remove fluoride, yields adequate fission-product decontamination.

Experimental work on development of an anion-exchange process for accomplishing purification of the Purex plant neptunium product has been concluded,<sup>4</sup> and a summary report is in preparation. The recommended procedure consists of the following steps (with Dowex-1 (X-4), 50- to 100-mesh resin):

1. Loading of Np(IV) at ambient temperature from a feed containing 6M nitric acid, ferrous sulfamate, and hydrazine, to an average of about 25 g of neptunium per liter of resin bed.

2. Washing at ambient temperature with 6M nitric acid containing ferrous sulfamate and hydrazine to remove plutonium. Laboratory results indicate plutonium decontamination factors of about 2000 with 15 column volumes and 6000 to 7000 with 20 column volumes of wash.

3. Washing at 60°C with 8M nitric acid, 0.01M hydrofluoric acid to remove fission products and UX<sub>1</sub>. Laboratory data indicate a zirconium-niobium decontamination factor of about 70,000 and a UX<sub>1</sub> decontamination factor of 500 to 1000 with 20 column volumes of wash.

4. Elution at ambient temperature with 0.35M nitric acid. Elution in fractions is advantageous since it enables the product to be recovered at a concentration of about 25 g of neptunium per liter. Recycle of perhaps the first 5 per cent of the eluted neptunium would enable significant additional UX<sub>1</sub> decontamination to be obtained also.

### Separation of Binary Mixtures

A single-pass method for the ion-exchange separation of binary mixtures of metals studied at Ames<sup>23</sup> consists in complexing each of the components in the mixture with a separate complexing agent at a pH sufficient to ensure maximum coordination of the metals. The complexing agents are chosen such that the metal complexes formed are of the opposite charge. The mixture is then passed through an ion-exchange resin which absorbs one species completely, allowing the other to be collected in the effluent. An anion- or cation-exchange resin is used. Sulfosalicylic acid was used to form a negative complex with iron, uranium, aluminum, thorium, zirconium, and yttrium. Ethylenediamine was used to form a positive complex with copper, zinc, nickel, or cadmium. Quantitative separations of binary mixtures containing one metal from each of these groups were performed at pH values 8, 9, and 10, using Dowex-50 (X12), NH<sub>4</sub> form (nuclear sulfonic cation-exchange resin), and Amberlite IRA-401 (quaternary amine anion-exchange resin).

### Volatility Processes

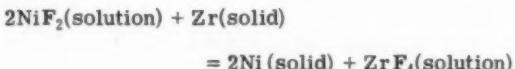
In fluoride volatility processes uranium is converted to the volatile hexafluoride which is decontaminated by distillation or absorption techniques. This Review includes information on fused-salt processing studies, ignitions of uranium in liquid bromine trifluoride, and the dissolution of metals in nitrogen dioxide-hydrogen fluoride solutions.

### Fused-salt Processing

The fused-salt process is being developed for enriched uranium-zirconium fuel alloys. Hot-cell equipment is under test at Oak Ridge National Laboratory. Several inactive runs have been made to develop remote operation techniques. The process consists in dissolving the zirconium-uranium fuel alloy by hydrofluorination at 650 to 700°C in fused 58 mole % lithium fluoride-42 mole % sodium fluoride, which reaches a final composition of 32 mole % lithium fluoride-23 mole % sodium fluoride-45 mole % zirconium fluoride. Uranium hexafluoride can then be volatilized from the fused salt by fluorination at temperatures of 450 to 500°C.<sup>16</sup> The temperature-solubility properties of this salt

mixture are evident from the phase diagram of the ternary system shown in Fig. 9. This ternary system and the binary system sodium fluoride-zirconium fluoride exhibit very similar process behaviors.

In the runs made to date positive indications of metallic nickel deposition have been observed. This presumably results from the reduction of nickel fluoride in the fused salt by the zirconium metal present or by hydrogen produced as the zirconium dissolves. This effect may reduce nickel corrosion during dissolution, particularly if an electrochemical cell is established, since the reaction



has a free energy change of -32 kcal/mole at 1000°K.

Some plugging of off-gas lines has occurred. A liquid hydrogen fluoride scrubber for the process off-gas is being developed. It consists of a packed tower with hydrogen fluoride condensate running countercurrent to the off-gas stream.<sup>24</sup>

The reaction rate of gaseous hydrogen fluoride with Zircaloy-2 in the temperature range 600 to 725°C is an order of magnitude higher for the gas-solid reaction than for fused-salt hydrofluorinations at corresponding temperatures. At 700°C, a piece of 1/2-in. Zircaloy-2 plate reacted uncontrollably with a 25 per cent hydrogen fluoride-75 per cent argon mixture. Reaction rates of the bare metal, obtained by extrapolation to zero reaction time, were 35, 17, and 8 mg/(min)(sq cm) at 725, 695, and 650°C, respectively, in 35 per cent hydrogen fluoride-65 per cent argon.<sup>25</sup>

In order to protect the walls of the fluorination vessels, frozen wall designs are being developed at Argonne National Laboratory. By providing an internal heat supply and cooling the outside wall, the thickness of the solid salt layer can be controlled. Small-scale tests with sodium fluoride-zirconium fluoride salt were made successfully in mock-up equipment with two different methods of internal heating. In one test, 350-kilocycle induction heating was used. To prevent molten salt from contacting the induction coil, a cooling grid was interposed between the coil and the molten salt which acted as a susceptor. The frozen salt layer was uniform

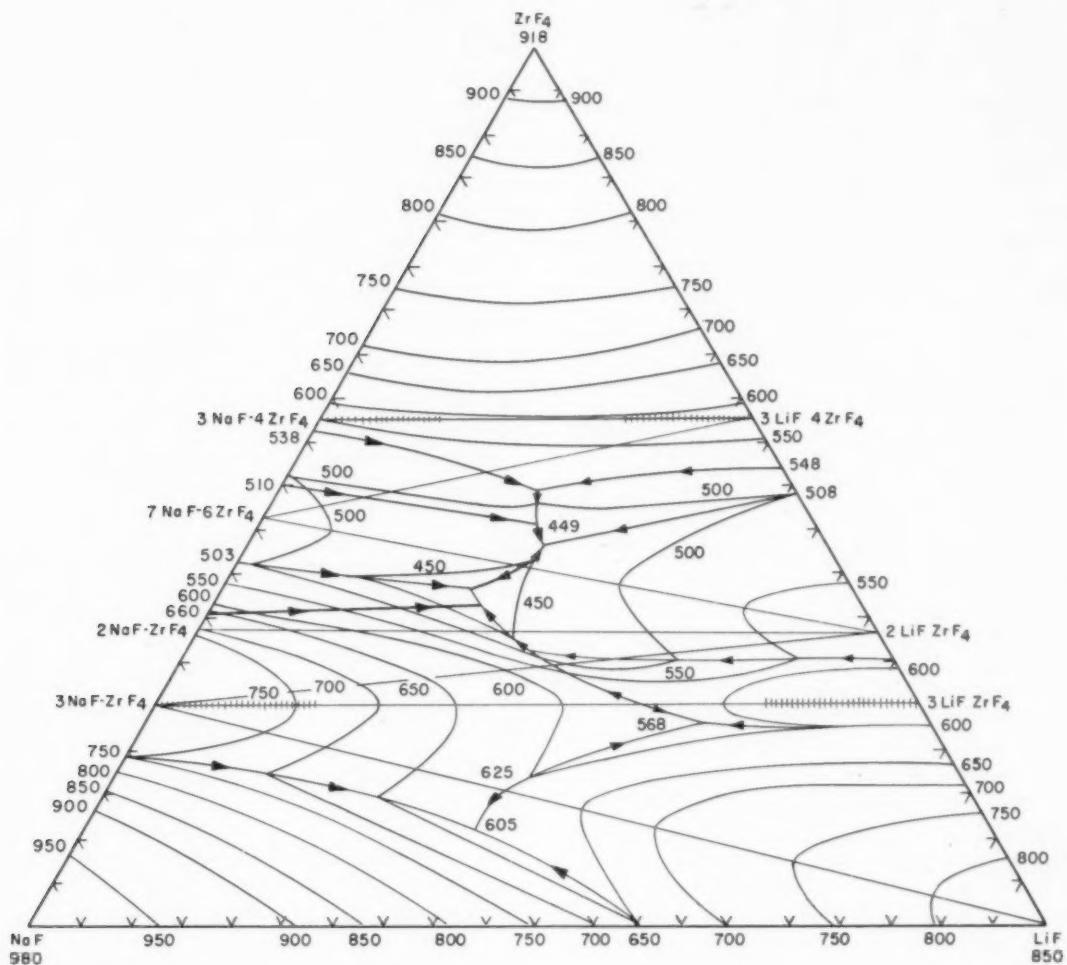


Figure 9.—The system  $\text{NaF}-\text{LiF}-\text{ZrF}_4$ . All temperatures are in degrees centigrade. Compositions are in mole %.  $\cdots\cdots$ , solid solution. (Oak Ridge National Laboratory, June 1958.) (Unpublished.)

along the vertical wall and its thickness was not influenced by sparging near the center of the melt. Once a steady state had been reached the system was stable, even with power fluctuation.<sup>26</sup>

In another test, electrodes were immersed in fused salt contained in a water-jacketed vessel. The shorting out of current between the electrodes near the surface of the melt, however, resulted in a thinner layer of frozen salt near the top of the vessel. A new type of electrode has been designed to minimize this tendency.<sup>26</sup>

A summary of laboratory studies on the Oak Ridge fused-salt process has been published.<sup>27</sup> A process for the fused-salt fluorination and

the sodium fluoride decontamination step is discussed along with the results of laboratory studies. Also mentioned in some detail are corrosion, the behavior of nickel fluoride suspensions, and basic chemical studies relating to the sodium fluoride adsorption step.

#### Ignition of Uranium in Bromine Trifluoride

Previously reported<sup>19</sup> studies at Brookhaven National Laboratory on the ignition of high surface area metallic uranium in bromine trifluoride systems have been continued. A technique has been developed wherein uranium samples

with high surface-to-volume ratios are exposed to liquid bromine trifluoride solutions without prior vapor contact.<sup>28</sup> This is accomplished by suspending the uranium sample in a basket immersed in liquid Freon-113 and then displacing the Freon by rapid introduction of bromine trifluoride. Oxide-coated surfaces and oxide-free surfaces of uranium have been compared. To prepare the oxide-free surfaces, the oxide coating was removed by pretreatment in a dilute solution of bromine trifluoride in Freon-113.

The results indicate that oxide-free uranium of high specific area (about 8.5 sq cm/g) will ignite at room temperature in bromine trifluoride solutions containing 2.0 to 5.5 mole % uranium hexafluoride. Ignitions have been initiated with the uranium entirely immersed. Uranium chips freed of surface oxide are essentially unreactive in pure bromine trifluoride and in solutions containing as much as 0.6 mole % uranium hexafluoride at metal temperatures up to 40°C; however, slightly oxidized uranium of high specific area is very reactive and will ignite in solutions containing 0 to 6 mole % uranium hexafluoride. With oxide-free surface, detonations were obtained in some cases at about 125°C in bromine trifluoride. Variations in behavior were found, depending on the fineness of chips or turnings and the source of the uranium. Although the ignition and detonation of finely divided BNL uranium were achieved after the uranium had been submerged in bromine trifluoride solutions and dissolution was in progress, a solid cylinder of this material as small as  $\frac{1}{4}$  in. by  $\frac{1}{4}$  in. could not be ignited.

#### **Nonaqueous Dissolutions in Nitrogen**

##### **Dioxide-Hydrogen Fluoride Solutions**

Experiments on the dissolution of Zircaloy and other metals in liquid anhydrous hydrogen fluoride media are in progress at Brookhaven.<sup>28</sup> Initial tests showed that Zircaloy-2 and zirconium-uranium alloys are dissolved at rapid initial rates in bromine trifluoride solutions containing nitrogen dioxide and hydrogen fluoride. Controlled dissolutions were performed at temperatures from 95 to 120°C, and an investigation of the zirconium complex was started. Uranium hexafluoride was volatilized from the dissolution mixture, although successive treatments of bromine trifluoride were necessary for efficient removal.

Zircaloy-2 is also dissolved by binary mixtures of nitrogen dioxide and hydrogen fluoride but not by either of the components separately. Dissolution rates of the order of 100 mg/(sq cm)(min) were obtained at 100°C in solutions containing 11 mole % nitrogen dioxide. Higher concentrations of nitrogen dioxide yielded higher rates.

The dissolution of 2S aluminum in 25 mole % nitrogen dioxide-75 mole % hydrogen fluoride proceeded at a penetration rate of 57 mils/hr in a test at reported temperatures of 121 to 178°C. Type 304 stainless steel dissolved in 56 mole % nitrogen dioxide-44 mole % hydrogen fluoride at a penetration rate of about 20 mils/hr at temperatures of 150 to 200°C. A Monel corrosion coupon showed negligible weight loss during the tests.

The addition of a small quantity of hydrogen fluoride was sufficient to cause the dissolution of Zircaloy-2 in liquid nitrogen dioxide. In a nitrogen dioxide solution containing 7 mole % hydrogen fluoride, the rate was 27 mg/(sq cm)(min) at 70°C.

#### ***Pyrometallurgical Processing***

Pyrometallurgical processes are under development for the undelayed processing of fissile and fertile materials discharged from reactors. Because they offer promise of reduced processing costs, their development is a part of the program to achieve economic nuclear power.

#### **Melt Refining**

The melt-refining process<sup>\*17</sup> will be employed in a plant adjacent to the Second Experimental Breeder Reactor (EBR-II) to enable rapid recycle of discharged fuel. Drawings and specifications for the Fuel Cycle Facility were submitted to prospective bidders around Apr. 1, 1959.<sup>29</sup> About one and a half years are being allowed for construction, which places the completion date at the end of 1960. Eight to twelve months will be consumed in equipment installation and testing, so that processing of irradiated material is scheduled to begin near the end of 1961.

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\*Irradiated fuel melted in a zirconia crucible and held molten for several hours, allowing purification to occur through vaporization and crucible reactions.

Contracts have been let for shielding windows and cranes, and procurement of other items is under way. A prototype, radiation-stable general purpose manipulator has been received and installed in a mock-up area which is being used to operate melt-refining equipment. A new melt-refining furnace has recently been installed in this area for operation in a manner simulating as close as possible that planned for the EBR-II facility.

A series of six 10-kg runs was made in the prototype EBR-II melt-refining furnace to study cerium removal.<sup>26</sup> In a lime-stabilized zirconia crucible and at a temperature of 1400°C, cerium, initially at a 0.4 per cent concentration was removed as follows: 85 per cent after 1½ hr, 95 per cent after 3½ hr, and greater than 99 per cent after 4½ hr. The results are about as predicted from smaller-scale experiments. The mechanisms of cerium removal by oxide formation in urania crucibles were recently investigated by Smith.<sup>30</sup>

A series of five 2-kg scale melt-refining experiments with "plutonium-fissium" alloys was completed without difficulty and with no spread of contamination.<sup>29</sup> Yields of purified metal were around 90 per cent, which, for this scale, are comparable to that obtained with a "uranium-fissium" alloy. Preliminary results show no significant plutonium enrichment in the slag relative to that in the metal phase. Cerium removals were essentially complete and comparable to those obtained with uranium-fissium.

A further investigation was made of the possible zirconium contamination of molten uranium and its cerium alloy resulting from prolonged holding at 1400°C in stabilized zirconia crucibles.<sup>29</sup> Zirconium pick-up in 5-, 9-, and 13-hr tests was negligible, amounting to only 20 ± 10 ppm in each test. It is fairly certain that the zirconia crucible will not constitute a source of zirconium contamination of a uranium melt.

The extent to which reactions may occur at high temperatures between zirconia and graphite (used as the induction heating susceptor) is an important factor in design of melting assemblies for the melt-refining process. Experiments at 1700°C showed considerable evolution of carbon monoxide as a result of reaction of zirconia with graphite.<sup>29</sup> Although conditions may be more extreme than in a plant furnace, the experiment indicates that the consequences of carbon monoxide evolution should be evaluated. A program for

investigating other susceptor-insulation combinations has been started.

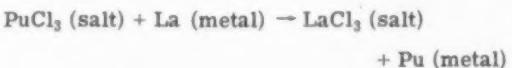
The Pyrometallurgical Refabrication Experiment is an engineering development for the remote processing and refabrication of irradiated fuel from Sodium Reactor Experiment (SRE) reactors. Information has been reported<sup>31,32</sup> on the equipment development, maintenance, and repair provisions for the oxide drossing process (synonymous with melt refining) and other cell equipment. The work has not been reoriented to processing oxide rather than metallic fuels.<sup>33</sup>

### Processing of Plutonium-rich Fuels

Results of studies of various pyrometallurgical methods for the processing of plutonium-rich fuels have recently been reported.<sup>34</sup> The studies were made on a 1-kg scale with synthetic spent fuel (fissium) alloys of plutonium containing 10 at.% iron. The methods studied were release or volatilization of gaseous or highly volatile fission products, oxide slagging (melt refining), halide slagging, and removal through solubility limitations (liquation).

Oxide slagging experiments show the usual retention of noble elements (zirconium, molybdenum, ruthenium, and the iron alloying agents) and the removal of the reactive rare earths (see Table III-2). Temperatures of around 1400°C are required for a reasonable rate of removal of rare earths. Cerium removal appears slower from a plutonium-rich fissium alloy than from uranium fissium alloys; data for the latter were reported in a previous Review.<sup>19</sup> In magnesia essentially complete removal was obtained after 8.3 hr at the expense of poor plutonium recovery. As in the case of the melt-refining process, zirconium was not introduced into solution, indicating that ZrO<sub>2</sub> is reduced to a lower oxide.

Chloride slagging at 600°C using a 77 wt.% PuCl<sub>3</sub>-NaCl eutectic alloy melting at 453°C<sup>34,35</sup> resulted in virtually complete removal of lanthanum and cerium in reasonable times (Table III-3). As would be expected the noble elements were retained in the metal phase. Use of this eutectic salt would provide a replenishing procedure by virtue of the following reaction:



Similar results were obtained with LiCl-KCl and NaCl-KCl salt systems to which magnesium

Table III-2 OXIDE SLAGGING OF PLUTONIUM-RICH ALLOYS\*†

Crucible	Temp., °C	Time, hr	Product concentration/feed concentration						Pu recovery, %
			Fe	Zr	Mo	Ru	Ce	La	
ZrO <sub>2</sub>	1000	4	1.01	1.00	1.04	1.01	0.99	0.97	99
ZrO <sub>2</sub>	1200	4	0.99	0.99	0.96	1.00	0.79	0.46	95
ZrO <sub>2</sub>	1400	4	1.02	0.98	1.09	0.99	0.39	0.03	91
ZrO <sub>2</sub>	1400	2	1.00	0.98	0.95	1.03	0.63	0.16	93
MgO	1400	2	0.90	0.93	0.95	1.01	0.57	0.40	>91
MgO	1400	5	1.02	0.98	0.98	1.07	0.40	0.13	93
MgO	1400	8.3	1.02	0.81	0.85	1.00	<0.006	<0.01	72

\*Data taken from reference 34.

†Initial composition (weight per cent): Pu-91.47, Fe-2.56, Zr-0.81, Mo-0.87, Ru-1.31, Ce-1.05, and La-1.93.

Table III-3 CHLORIDE SLAGGING OF PLUTONIUM-RICH ALLOYS<sup>35</sup>Alloy composition: Same as Table III-2  
Salt composition: 77% PuCl<sub>3</sub>-NaCl eutectic

Equilibration time, hr	Product concentration/feed concentration				
	Fe	Mo	Ru	Ce	La
3	0.93	1.0	0.96	<0.009	<0.04
6	0.94	0.9	0.99	<0.01	<0.04
30	0.97	0.9	0.94	<0.01	<0.04

chloride was added as the slagging agent in amounts slightly in excess of the stoichiometric quantity. Large excesses resulted in some plutonium transfer to the salt phase and these were avoided. Complete transfer of rare-earth elements took place in 1 hr or less. A number of other salt compositions can presumably be used to vary the melting point as desired.

The extraction of plutonium from neutron-irradiated uranium by a uranium trichloride and magnesium chloride mixture was examined by McKenzie, Elsdon, and Fletcher.<sup>36</sup> The results with uranium trichloride were used to calculate the free energy change for the reaction:



These results were used to predict the plutonium extraction by magnesium chloride on the assumption that the above equilibrium is established through formation of uranium trichloride by the reaction:



Reasonable agreement between predicted and experimental results was realized.

Pyrochemical methods under study at Hanford for recycling and reconstituting plutonium-aluminum alloys and for the separation of plutonium for ceramic type uranium oxide fuel elements were recently reported.<sup>37</sup> For the plutonium-aluminum alloys reconcentration of plutonium may be accomplished by addition of new plutonium or by removal of aluminum. Fission-product decontamination is secondary. One method of adding plutonium is as plutonium oxide using the cryolite process. Cryolite (Na<sub>3</sub>AlF<sub>6</sub>) serves to dissolve the plutonium oxide and also the aluminum oxide reduction product which results from reduction of plutonium oxide by aluminum. Some decontamination is achieved by extraction of fission products into the salt flux. Methods of aluminum removal which have been tried involve partial oxidation of the aluminum and dissolution of the oxide in cryolite or the formation of volatile aluminum halides (AlCl<sub>3</sub> or AlF<sub>3</sub>).

The type of process under investigation for recovery of plutonium from UO<sub>2</sub> fuels involves dissolution in fused-salt systems, followed by reduction and distribution of materials of interest between salt and metal phases. The double salt, KAlCl<sub>4</sub>, melting at 260°C readily dissolves uranium and plutonium metals and oxides (yielding Al<sub>2</sub>O<sub>3</sub> in the case of oxides) and may be employed up to 800°C before its vapor pressure becomes appreciable. When an aluminum metal phase is present, plutonium remains predominantly in the salt phase, while uranium favors the metal phase, thus affording a means of separation.

#### Processing of Ceramic Fuels

In previous reviews, work of Atomics International has been reported on chemical pulveri-

zation of uranium oxide pellets by alternate oxygen-oxidation and hydrogen-reduction cycles at 375 to 1100°C. This work was recently summarized by Strausberg, Luebben, Rosen, and Murbach.<sup>38</sup> Fission-product studies have shown that most of the cerium, ruthenium, tellurium, iodine, and probably rare gases can be removed by this process. Studies have been started on refabrication of oxide shapes. Significant increase in the densities of refabricated UO<sub>2</sub> pellets was achieved by a second oxidation-reduction cycle of the powder (94 to 97 per cent of theoretical as contrasted with 88 to 93 per cent obtained after a single oxidation-reduction cycle).

A program within the Processing Refabrication Experiment has been proposed<sup>33,39</sup> in which equipment, methods, and techniques for remote, low-decontamination processing and reconstitution of highly irradiated and short-cooled UO<sub>2</sub> fuel are described. The major function of such processing is replacement of fissionable material and repair of irradiation damage. The major objective of such a large-scale engineering experiment is to establish the feasibility and economics of the low-decontamination processing of oxide fuels.

This general concept has been extended to processing of carbide fuels by reacting the fuel with oxygen to produce UO<sub>2</sub> and subsequent conversion back to UC by reaction with carbon.<sup>40</sup> In an experiment in which irradiated UO<sub>2</sub> was converted to carbide, the final temperature being 2200°C, appreciable removal of cesium, cerium, and other rare-earth activities was realized.

#### Liquid-metal Processes

Increasing attention is being given to processing of nuclear fuel materials in various liquid-metal solutions at several atomic energy sites. Purification mechanisms which can be used are selective oxidation or reduction, fractional crystallization, extraction with immiscible molten metals or salts, and distillation. The metals which have been generally used as solvents for uranium and plutonium are aluminum, magnesium, mercury, zinc, and cadmium.

A number of papers were presented at the April meeting of the American Chemical Society relative to the characteristics of liquid metal solvent media. Subjects reported on at this meeting are as follows:

1. Solubilities of nuclear materials and various fission elements in zinc, magnesium, and cadmium, and various mixtures of these.<sup>41</sup>

2. Coprecipitation phenomena in liquid-metal systems.<sup>42</sup> Coprecipitation of trace elements with carrier precipitates in zinc and cadmium systems was found to follow the logarithmic distribution law of Doerner and Hoskins. This constitutes the first verification of this law for liquid-metal systems.

3. Rate of reaction of uranium with liquid zinc.<sup>43</sup>

4. Thermodynamic functions for the uranium-zinc system.<sup>44</sup>

5. Decontamination of irradiated fuels by utilizing liquid-metal solvents.<sup>45</sup>

6. Problems in fabricating and operating a circulating molten-metal system.<sup>46</sup> Although discussed from the standpoint of a molten-metal fuel reactor, problems of corrosion, heat and mass transfer, pumping, and design and fabrication are similar to those which would be encountered in processing equipment.

Considerable effort is being devoted at ANL to the development of liquid-metal processes for the specific applications of: (1) recovery and some decontamination of fissionable materials in melt-refining process residues (crucible skulls), and (2) isolation of plutonium from uranium blanket materials. Cadmium-based solvents rather than zinc-based solvents are now receiving principal attention<sup>29</sup> because the less corrosive nature of cadmium permits containment in equipment constructed of rather common metals (mild steel and various 400 series stainless steels). Only graphite, silicon carbide, and various oxide refractories are suitable for extended containment of zinc systems at the temperatures of interest (up to 800°C).

Several separations in liquid-metal processes are based on the insolubility of uranium in magnesium or magnesium-rich alloys and the contrasting relatively high solubilities of other elements in magnesium, e.g., plutonium, thorium, and rare earths. The plutonium-uranium separation is the basis of most blanket processes; the thorium-uranium separation, first reported by Chiotti and Shoemaker,<sup>47</sup> may be used to separate U<sup>233</sup>; equipment for this purpose is now being developed at Atomics International.<sup>48</sup>

Magnesium is a good reducing agent and may be employed in solution in cadmium, mercury, zinc, etc., to reduce oxides of uranium and plu-

tonium. It has been used frequently in zinc for reduction of  $\text{UO}_2$ . Oak Ridge has recently reported virtually 100 per cent reduction of 1700°C-fired  $\text{UO}_2$  powder by magnesium dissolved in mercury in the presence of magnesium chloride flux.<sup>48</sup> Similar reductions have been made by magnesium dissolved in cadmium.<sup>29</sup>

### Miscellaneous

A Russian article<sup>49</sup> discusses fundamental studies on plutonium, uranium, and their alloys. The studies reported include: the characteristics of metallic plutonium and its behavior with other elements from the standpoint of their position in the periodic table; uranium and its behavior under thermal cycling and under exposures to radiation in relation to alloying, thermal, and mechanical treatments; methods of fabrication of uranium by pressure forming; effects of neutron exposure on the structures and properties of the alloys.

Reprocessing by pyrometallurgical and aqueous methods were compared and preliminary cost estimates made for two types of fuel recycle (uranium-plutonium and thorium- $\text{U}^{233}$ ).<sup>50</sup> It was stated that "Pyroprocessing methods with relatively low costs, sufficiently small losses, and plant design flexibility appear attractive when applied to fuel recycles. The shorter time between fuel reprocessing is particularly attractive to thorium recycle because it eliminates a difficult handling problem."

Three pseudobinary systems of uranium carbide with tantalum carbide, zirconium carbide, and niobium carbide were examined.<sup>51</sup> A complete range of solid solutions exists for each system.

Thermal expansion data have been reported from 1000°C to points of permanent deformation for  $\text{Al}_2\text{O}_3$ ,  $\text{BeO}$ ,  $\text{MgO}$ ,  $\text{B}_4\text{C}$ ,  $\text{SiC}$ , and  $\text{TiC}$ .<sup>52</sup>

### *Homogeneous Reactor Processing*

The Homogeneous Reactor is useful from the standpoint of chemical processing. One of its advantages is the ability to remove a side stream from the reactor, process it and return it to the main loop, where such continuous processing is employed; the decontamination requirements need not be high.

A report on an absorption process for the recovery of fission-product noble gases as a sub-

stitute for charcoal traps has appeared in the last quarter.<sup>53</sup> The subject is of significance for homogeneous reactors, pyrometallurgical processing operations, and chemical process dissolutions. The incentive to pursue the absorption process is associated with the inherent disadvantages of charcoal absorbers which include batch operation requiring constant attention and complicated valving arrangements, operation at very low temperatures, small amounts of moisture tend to decrease capacity, and the danger of possible uncontrollable combustion resulting from radiolytic oxygen present. Solubilities of xenon and krypton in a large number of organic materials were measured. The data are correlated in terms of a solid cohesive density and these were found to conform to the solubility theory of Hildebrand. Solubilities in general decrease with increasing temperature to 150°C and follow Henry's law. The design of an absorption-stripping process is presented.

Operation of the Homogeneous Reactor Test (HRT) chemical processing plant has continued. The corrosion products separated by the hydroclone remain reasonably constant in analysis: 22 per cent iron, 46 per cent zirconium, 3.4 per cent chromium, and 1 per cent titanium. Difficulties have been experienced however in determining the uranium content of these solids. Considerable variation has been observed. Testing of an electrolytic method for removing nickel from simulated HRT fuels has continued. Under proper conditions with a mercury cathode, manganese as well as nickel can be removed.<sup>16,54,55</sup>

A study has been made of the various types of insoluble salts that occur in an aqueous homogeneous reactor and their behavior at operating conditions. The classes of salts considered include the rare-earth sulfates, salts with inverse temperature dependent solubility, and the insoluble salts formed in the solution such as corrosion product oxides. In general, it was concluded that the rare-earth sulfates were deposited in the hottest points of the system. Those fission products and corrosion products which are insoluble at all temperatures will, in general, deposit on any surface regardless of temperature. The study revealed that quantitative predictions for the HRT chemical processing plant were difficult due to variables that could not be evaluated.<sup>56</sup>

## Instrumentation and Equipment Development

The measurement of flow of gaseous uranium hexafluoride by a Hastings flowmeter has been reported.<sup>57</sup> The instrument operates by measuring the temperatures of two noble metal thermocouples suspended in the gas stream, one of which is heated by a constant power source. The temperature difference of the two thermocouples is directly related to the rate of flow of the gas. Additional developmental work should make the instrument applicable for the accurate measurement of the flow of uranium hexafluoride gas.

The development of a scintillation counter which measures the alpha activity in a process stream has been reported.<sup>58</sup> The alpha activity in an aqueous plutonium stream was detected by a ZnS(Ag) phosphor located in the stream; a thin Teflon film was placed between the phosphor and the stream to protect the phosphor from contamination and chemical attack. A linear relationship was found between the scintillation net count rate and the activity of the solution. The background depends upon the maximum activity that has been monitored and appears to be due to plutonium adsorption on the Teflon film. Pre-exposing the film to a solution whose activity is the maximum within the range to be monitored ( $10^3$  to  $10^7$  disintegrations/min/ml) fixes the background level. The background level then accounts for less than 1 per cent of the total count rate observed with this solution. Calibrations were found to be reproducible within less than  $\pm 10$  per cent.

A gamma-sensitive scintillation detector has been developed which will determine the location of a free surface of a radioactive liquid with an accuracy greater than  $\pm 0.05$  in.<sup>59</sup>

## Corrosion

Corrosion is a subject which is an integral part of each process development program. Many of the current developments involve the use of chemicals which are more than usually corrosive, and in many instances programs have been set up to solve the resulting materials of construction problems. In this section an attempt will be made to cover the progress on such

programs which has occurred in the past three to six months.

### Solvent Extraction

The Darex process is designed to adapt the processing of stainless-steel matrix fuels to existing solvent-extraction plants. Corrosion programs at both ORNL (through BMI) and Hanford have shown that titanium is probably best able to withstand the corrosive dissolution environment consisting of 5M nitric acid-2M hydrochloric acid. Efforts are being made to evaluate the use of titanium in heat-transfer service by steam heating titanium tubes submerged in the dissolution environment. In general, little attack has been observed. However, several defects in the form of fissures and crevices in critical areas have been observed. These are attributed to the initial condition of the metal rather than to the corrosive environment. Results reported include exposures from 660 to 2000 hr.<sup>60,61</sup>

Low carbon Hastelloy F has been tested at Hanford for possible Darex application. After 100 hr of exposure to a variety of conditions in the pilot-plant dissolver, corrosion rates of 4 and 2 mils/month were observed in the liquid and vapor phases, respectively. Some intergranular attack was observed, but there was no preferential weld corrosion.<sup>4,62</sup>

The Sulfex process has also been designed to handle stainless-steel matrix fuels particularly where the cores of such fuels consist of  $UO_2$ - $ThO_2$ . It is proposed to use the Sulfex process in conjunction with the Thorex process. A compilation of corrosion information on this system was included in the preceding Review.<sup>20</sup> Verification of such data together with further discussion is included in more recent reports.<sup>63,64</sup>

Some new data are presented on the corrosion of Hastelloy F in 4M sulfuric acid under heat-transfer conditions (metal temperature, 140°C). The measured corrosion rates of 100 mils/month or greater were found to reduce to 10 mils/month in the presence of stainless-steel dissolution products.<sup>65</sup> Unstabilized Carpenter 20 continues to show a considerable sensitivity to cracking and pitting type phenomena.<sup>65,66</sup> Coupons bent to a sharp angle of 60 deg and exposed to boiling 4M sulfuric acid showed considerable cracking on the inside diameter of the bend but little on the outside diameter. Information from Battelle indicates that cracking of stabilized

Carpenter 20 can be inhibited by the presence of dissolved stainless steel. Heat-treatment is also beneficial.

Nionel continues to be one of the promising materials which could be useful in both Sulfex and Thorex environments. It is reported that the presence of metallic stainless steel in the Sulfex decladding environment decreases the corrosion rate, whereas dissolved stainless steel increases it.<sup>62</sup>

A third process for the decladding and dissolution of stainless-steel matrix fuels is the Niflex process which utilizes mixtures of hydrofluoric and nitric acids. A Niflex pilot plant dissolver made of Hastelloy F has been installed at Hanford. A section of weld removed from the unit was subjected to a corrosion test in boiling 1M nitric acid-2M hydrofluoric acid. The measured corrosion rate was about 200 mils/month. The result is interpreted as meaning that the annealing of the unit has been only partially completed.<sup>62</sup>

A program is under way to develop a modified Hastelloy F composition which would be less sensitive to preferential weld metal attack. One such alloy in which the molybdenum content was increased from 6 to 9 per cent and containing no niobium appeared to be considerably better than the reference alloy.<sup>21,62</sup>

The Idaho Chemical Processing Plant (ICPP) is studying the containment of nitric and hydrofluoric acid mixtures. Types 309 and 316 stainless steels, Carpenter 20, Hastelloy F, and Incoloy 804 were tested in 1M to 8M hydrofluoric acid and 1M to 13M nitric acid. Corrosion in all cases was very high (100 to 300 mils/month) and additions of aluminum ion to the extent of 0.5M did not appreciably affect the results.<sup>65</sup>

Several procedures have been suggested as possibilities for the head-end processing of zirconium matrix fuels. Included among these are the Zirflex and Zircex processes. In the Zirflex process, the fuel would be dissolved in 3M  $\text{NH}_4\text{-HF}_2$  or 6M  $\text{NH}_4\text{F}$ -1M  $\text{NH}_4\text{NO}_3$ . The former environment used at the boiling temperature has been found to be excessively corrosive to stainless steel type 304L, Hastelloy F, and Carpenter 20 (25 to 175 mils/month). In the latter environment at the boiling point, type 309 Cb stainless steel was found to have a corrosion rate of 8.5 mils/month.<sup>25</sup> Rates up to 12 mils/month were reported<sup>61</sup> for type 347.

A status report about the development of the Zircex process has recently appeared. The

Zircex process utilizes a high-temperature chlorination of zirconium fuels followed by core dissolution in nitric acid. Table III-4 summarizes the materials considered useful for the procedure.<sup>66</sup>

Table III-4 MATERIALS OF CONSTRUCTION  
CONSIDERED SATISFACTORY FOR THE  
ZIRCEX PROCESS<sup>66</sup>

Hydrochlorinator*	Core dissolution†	Cyclic exposure‡
Inconel	Tantalum	Haynes 25
Haynes 25	Titanium	S-816
S-816	Vitallium	
Illiun R	Haynes 25	
Hastelloy B	S-816	

\*HCl,  $\text{ZrCl}_4$ ,  $\text{H}_2$  at 600°C; no weight losses observed.  
†0.4M  $\text{UCl}_4$ , 0.5M to 5.0M  $\text{HNO}_3$ , reflux; 2 mils/month.  
‡11-hr hydrochlorination, 2-hr dissolution; dimensional change: 3 to 10 mils/year; severe intergranular attack.

#### Miscellaneous Aqueous Corrosion

A topical report on the corrosion of various materials of construction in fluoride solutions has appeared. A tabulation on the effect of temperature in 4M hydrofluoric acid for the five most promising alloys is shown in Table III-5.<sup>67</sup> Pretreatment of Carpenter-20 with 10M nitric acid at 100°C appeared to reduce the attack when subsequently exposed to the hydrofluoric acid

Table III-5 EFFECT OF TEMPERATURE ON  
CORROSION OF ALLOYS BY 4M HF

Alloy	Corrosion, mils/year		
	25°C	45°C	65°C
Stainless 309 Cb	40	448	508
Carpenter 20	18	10	64
Chlorimet 3	15	21	33
Durimet 20	5	8	55
Durco D-10	4	6	13

\*Data taken from reference 67.

environment. The period of time during which such "passivation" is effective was not determined. Table III-6 shows the effect of varying fluoride concentrations in a reference nitric acid environment at 70°C. The corrosion in mixed acids was found to be very high. At 40°C, stainless steel 309 Cb corroded with 4M hydrofluoric acid-10M nitric acid at a rate of 80 mils/year. At 80°C the rate was 125 mils/year. The corresponding rates for Carpenter 20 were

Table III-6 EFFECT OF FLUORIDE CONTENT ON CORROSION OF STAINLESS STEEL IN 8.33M NITRIC ACID AT 70°C<sup>67</sup>

HF conc., moles/liter	Corrosion, mils/yr	
	Stainless 309 Cb	Carpenter 20
0	6	4
0.03	27	36
0.13	82	114
0.26	100	174
0.79	205	509
1.58	298	851

320 and 335 mils/year. Ferric ion did not have an inhibiting effect on the corrosion of these alloys.

The behavior of 316 ELC stainless steel, both welded and unwelded, was studied in zirconium process waste solutions containing fluoride ion. The results indicated that fabrication is the greatest single factor affecting the possible life of a storage vessel made of this material. Pitting was common and was found to be largely dependent on the composition of the weld deposit, the welding process used, and whether or not the material had been properly heat-treated. Lowering the test temperature to 100°F from 150°F resulted in a notable decrease in the pitting attack. Heliarc welding was found to produce better welds than metal arc weld deposits. The combination of sensitized material with heavily stressed areas appeared to be particularly conducive to high rates of local attack.<sup>68</sup>

### Volatility Processing

In the fused-salt volatility process zirconium fuel is immersed in a molten fluoride melt which is sparged with anhydrous hydrogen fluoride. In a second step, fluorine is passed through the melt to convert the soluble uranium tetrafluoride to the volatile uranium hexafluoride. The latter is recovered and purified by distillation or absorption techniques.

Among the promising materials of construction for the first step of the process are nickel-molybdenum alloys such as INOR-1, INOR-8, Hastelloy B, and Hastelloy W. With fluoride melts consisting of sodium fluoride and zirconium fluoride, three general observations are made: (1) increasing the temperature from 650 to 700°C increases the over-all corrosion rates on the three nickel-molybdenum alloys markedly, (2) the zone of maximum attack is, in nearly all cases, at the melt-vapor interface, and (3) the

addition of 2.4 wt.% hydrogen to the hydrogen fluoride lowers the corrosion rate by factors of 3 to 12. In general, exposures at 650°C in the presence of hydrogen result in a maximum corrosion rate of 1 mil/month. At 700°C with no hydrogen present, corrosion rates are 17, 13, and 3 mils/month for INOR-1, INOR-8, and Hastelloy B. Silver was tested in a single exposure at 650°C without hydrogen present and the corrosion resistance was found to be no better than the INOR alloys.<sup>69,70,71</sup>

Another possible fluoride salt composition that may be useful in the process is 43 mole % sodium fluoride-57 mole % lithium fluoride. Two tests were made at 700°C; one without hydrogen and one with hydrogen. Severe interface corrosion was observed on all specimens tested, including INOR-1, INOR-8, Hastelloy B, and Hastelloy W. The presence of hydrogen in the one test did not appear to have reduced the attack in the liquid phase but some improvement was noted in the vapor phase specimens.<sup>70</sup>

A report on the current status of the fused fluoride volatility process at ORNL<sup>71</sup> includes some corrosion observations. The salt used was 50-46-4 mole % NaF-ZrF<sub>4</sub>-UF<sub>4</sub>. Total exposure time to fluorine sparge was estimated at 30 hr. The corrosion on three coupons of A- and L-nickel, both welded and unwelded, was reasonably uniform and low and was of the solution type. Assuming a uniform rate of attack the corrosion calculated from weight loss data is of the order of 4 mils. The nickel fluorine inlet tube and the reaction vessel itself showed corrosive attack of 4 to 9 mils in both liquid and gas zones. No evidence of intergranular attack was reported.

### Pyrometallurgical Processing

The containment of molten plutonium and uranium is a difficult though not insurmountable problem. In the development of the LAMPRE reactor at Los Alamos, a corrosion testing program for the containment of molten plutonium is under way. It had been observed earlier that the resistance of tantalum to this environment may be a function of its purity. Consistently better results have been obtained with high purity materials. In addition, the effect of cold work is very marked. Thoroughly annealed tantalum is attacked rapidly at 700°C while a similar piece heavily cold worked, remains unattacked at 800°C.<sup>72</sup>

Ames Laboratory has determined that yttrium has reasonably good resistance to molten uranium at 1200°C. Considerable effort is being directed at studying the fabrication characteristics of yttrium. It has been found, for instance, that cold rolling becomes increasingly possible as the thickness of the metal rolled is decreased. However, the resulting metal was found to be very brittle and subject to cracking; this was due to hard nonmetallic inclusions in the metal. The brittleness and hardness were accompanied by increasing hardness which could be reduced to original values by annealing at 800°C. The inclusions were identified by X-ray diffraction as yttrium oxide.

A yttrium metal loop has been assembled to study the corrosion characteristics of uranium-5 per cent chromium eutectic. In order to prevent oxidation of the yttrium, the loop was encased in a sheet of stainless steel type 446. A spacer of tantalum was placed between the two metals to avoid possible intermetallic effects.<sup>73,74</sup>

#### Miscellaneous

Fluid-bed calcination of aqueous process wastes is being studied at the ICPP. Stainless-steel wire mesh is inserted in the off-gas of such a unit to provide absorption surfaces for ruthenium. Corrosion tests at 550°C have indicated that type 304 stainless steel has a reasonably low rate of attack for this application.<sup>65</sup>

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### *Volume Reduction*

The Hanford pilot plant unit for the formaldehyde destruction of nitric acid mentioned in an earlier Review<sup>1</sup> has demonstrated that the reaction proceeds smoothly and is easily controlled. Cold formaldehyde and nitric acid were mixed in the reactor and after a  $\frac{1}{2}$ -hr delay period the reactor was heated. The maximum pressure generated was 1.7 psig with an initial mixture of 4.6M nitric acid and 1.4M formaldehyde.<sup>2</sup>

The pilot-plant investigation was concluded with a few scouting experiments to determine the effects of packed tower height, methanol concentration in the feed, and the applicability of the process to nitrate destruction in Darex effluents. Increasing the packed tower height from  $2\frac{1}{2}$  to 5 ft increased formaldehyde utilization by about 10 per cent. Increasing the methanol content of the formaldehyde from 10 per cent (normal) to 20 per cent increased effective formaldehyde utilization by another 5 per cent.<sup>3</sup>

Batch operations on Darex effluents showed no significant difference from similar operations on synthetic Purex waste. The free acid in solutions of either composition could be reduced to near zero with an over-all formaldehyde utilization efficiency of about 1.8 to 1.9 moles of nitrate per mole of formaldehyde.

Based on these observations it is believed that this process can be used for any application where it is desirable to reduce nitric acid concentration. It is particularly attractive when it is undesirable to neutralize excess acid with caustic.<sup>4</sup>

### *Reduction to Solids*

Work is reported on the adsorption of activity onto clays and glasses and on several methods of calcining liquid wastes.

#### **Adsorption of Activity on Natural Materials**

At Hanford a study of melting temperatures of the glasses formed by adding phosphate and

borate to Purex waste to form phosphate-borate glasses is in progress.<sup>2</sup> Glasses that can be handled in mild steel equipment require melting points less than 900°C if a protective atmosphere is used and less than 750°C in air. Over a fairly wide composition range the glasses will melt in this temperature range. One mixture, 13.7 per cent AlPO<sub>4</sub>, 10 per cent FePO<sub>4</sub>, and 76.3 per cent NaBO<sub>2</sub>, gave evidence of melting at the abnormally low temperature of 450°C.

#### **Calcination of Wastes**

The Hanford 8-in. radiant heat spray calciner referred to in a previous Review<sup>1</sup> has been put into operation.<sup>4</sup> The electrical resistance heating, the most novel feature of the design, was found to work well. The first run with simulated waste solution had to be terminated due to calcination of feed solution in the atomizing nozzle. The nozzle has been relocated.\*

Argonne National Laboratory has agreed to perform scouting calcination studies on synthetic Purex waste in the 6-in. fluid-bed waste calciner described previously.<sup>5</sup> These studies are planned to provide further data to aid the design of pilot-plant equipment and experiments for the proposed fluid-bed unit at Hanford.<sup>4</sup>

For the past four years a calcining apparatus of the rotary ball kiln type with dust controlled by condensation and absorption of the off-gases has been under development at Brookhaven National Laboratory.<sup>6</sup> A flow sheet of this process is shown in Fig. 10 and the calciner is shown in more detail in Fig. 11. At least four alloys

\*Later information from Hanford discloses that a series of runs has been made with generally satisfactory results. Both air and steam atomization have been used successfully. The wastes calcined have included acid Purex waste, Purex waste with phosphate addition (to form a low-melting glass), and neutralized Purex waste (with and without additions). Addition of sugar reduced the power load required and aided destruction of sodium nitrate. Build-up of solids on the wall of the calciner near the nozzle was a problem with some feeds but was largely eliminated by proper choice of operating conditions.

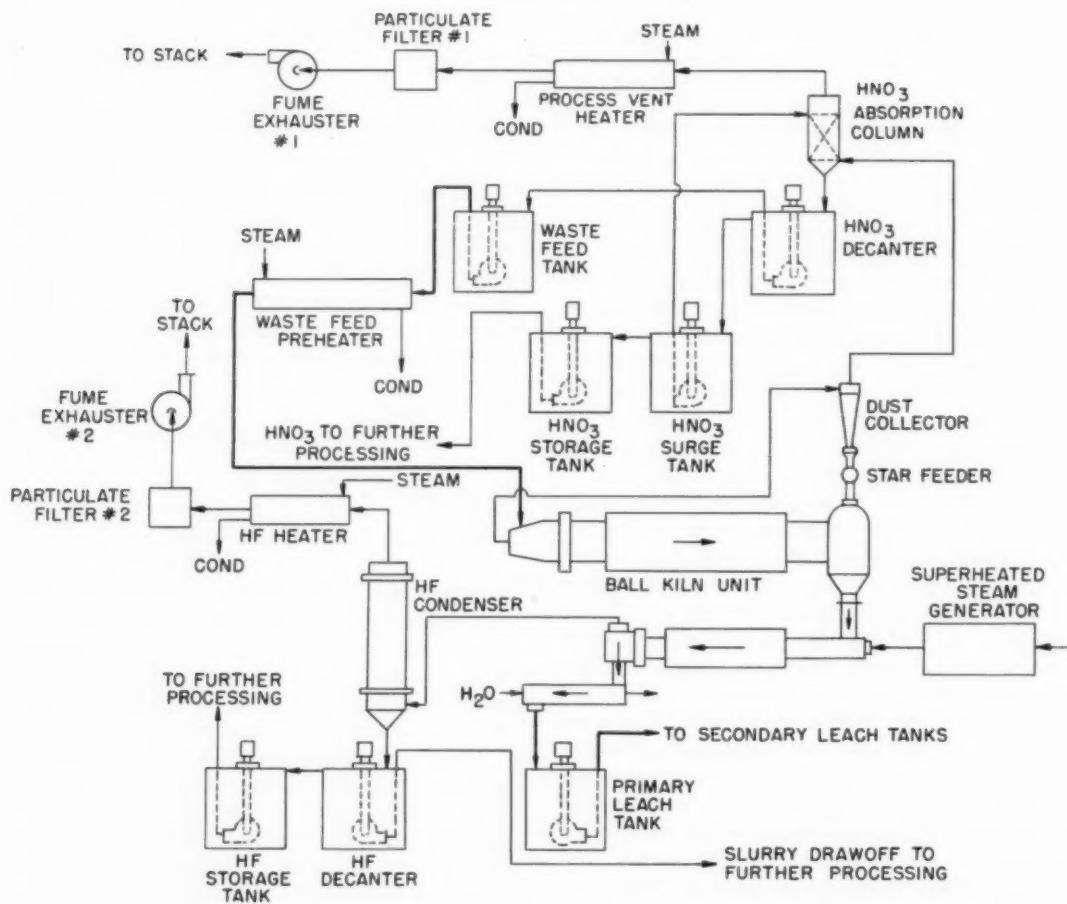


Figure 10—Schematic diagram of waste calcination and gas recovery system.<sup>6</sup>

are probably suitable as construction material for the high-temperature calciner vessel: Illium G, Inconel X, Haynes 25, and Nionel. It is concluded that calcination in rotary ball kilns appears to be practical with respect to product quality, mechanical design, off-gas volume, and dust carry-over.

At Idaho, the pilot-plant fluid-bed calciner was operated for about 500 hr during which time the sodium-potassium heating system was operated in the 1000 to 1300°F range. Excellent control of the feed rate has been achieved by installing a filter in the feed line ahead of the controllers.<sup>7</sup>

Samples of calcined waste containing one part of radioactive ICPP waste to 500 parts of synthetic waste (prepared at ANL by fluid-bed calcination at 500°C) were leached with 0.5M nitric acid solution in an attempt to remove the heat-producing and long-lived fission products.<sup>8</sup>

Greater than 90 per cent of the Cs<sup>137</sup>, approximately 67 per cent of the Sr<sup>90</sup>, and 9 per cent of the Ce<sup>144</sup> were removed from the calcined solid by six successive extractions at 25°C. In addition, 15 to 20 per cent of the initial solids, constituting all of the sodium nitrate and part of the aluminum oxide, were dissolved during leaching. In separate experiments less than 20 per cent of the Ru<sup>106</sup> and 10 per cent or less of the Zr<sup>95</sup> and Pu<sup>239</sup> were removed by six successive extractions. In general, only about 10 to 20 per cent of the heat producing fission products in 120-day cooled waste appeared to be readily extractable by leaching.

As a possible solution to the problem of heat removal from stored calcined waste, a scheme for circulation of calcine was studied which involved the slow circulation of the calcine using air to operate an airlift. An attrition test made

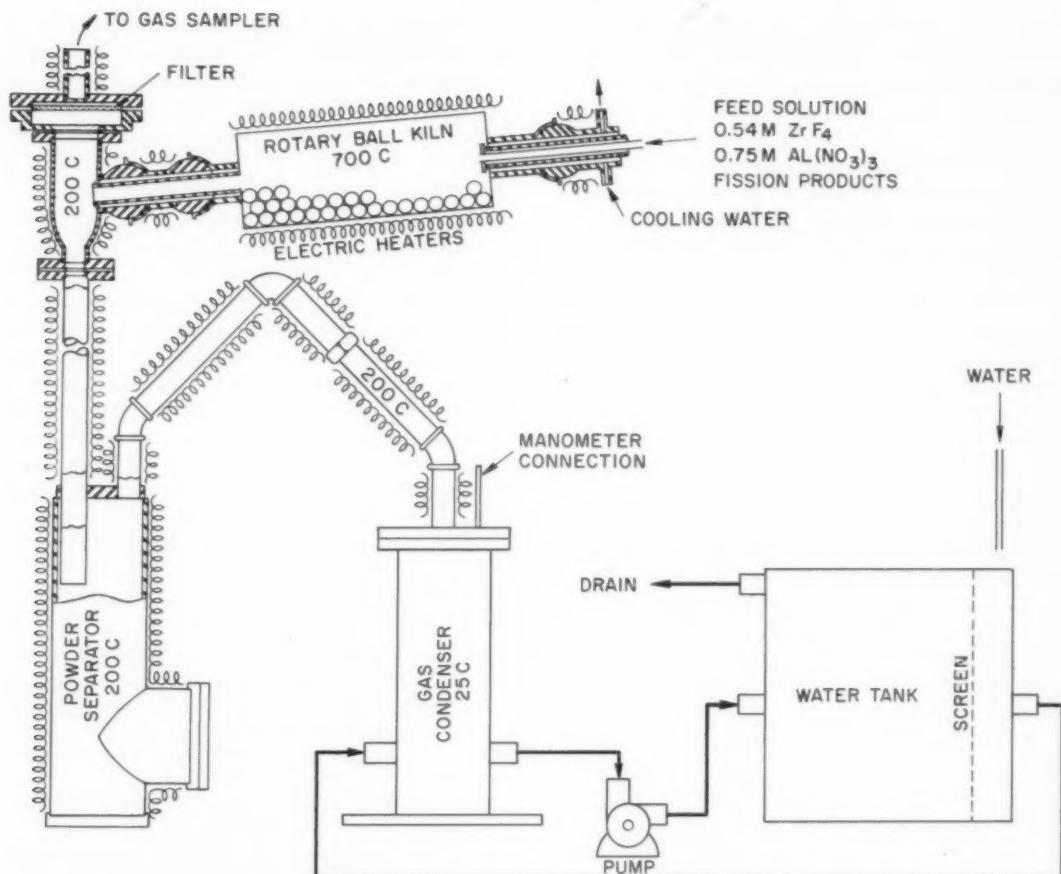


Figure 11—Single kiln calciner.<sup>6</sup>

on simulated ICPP calcine indicated an excessive fines build-up. Calcine below 60-mesh increased from 2.5 to 19 per cent in a 189-day test.<sup>9</sup>

### *Final Disposal Methods*

Two literature searches have been reported since the last Review. One<sup>10</sup> includes 23 references to classified and unclassified reports on the migration of plutonium and fission-product wastes in soils and ground water. Information on soil column and well logging techniques is also included. There is a short summary of each of the documents referenced. The second<sup>11</sup> contains 100 references to journal articles and unclassified and classified reports on radioactivity in the oceans. The ultimate fate and effect of arti-

ficial isotopes in the marine environment is considered. Also covered are physical processes of mixing, dispersion and dilution, the effect on all forms of biota and the effects of biota toward reconcentration. Sources of the radioactivity include that from weapons tests and from radioactive wastes.

The International Atomic Energy Agency's *ad hoc* panel on radioactive waste disposal in the seas met in Vienna in December 1958, under the chairmanship of Dr. Harry Brynielsson, Director General of the Swedish Atomic Energy Co.<sup>12</sup> In a statement issued at the conclusion of the meeting, the panel said that it had decided to establish working parties which in cooperation with the IAEA staff will assemble information and analyze available data in the fields of radioactive waste treatment, oceanography, marine biology, protection of fisheries and radiobiology.

They will also examine the need for additional research work. The results of the working parties will be submitted to the full panel, which "hopes to complete its task in the course of 1959" with the preparation of a report and recommendations which might serve as the basis for an international agreement on waste disposal.

At Hanford, disposal of certain wastes to the ground at shallow depth has long been practiced. It has been thought that the uptake of Sr<sup>90</sup> by the soil was pH dependent and that it was favored by an alkaline environment. Consequently, certain acidic Purex streams have been neutralized with limestone prior to cribbing. The indication of an unusually low capacity for this particular cribbing operation led to a series of experiments<sup>13</sup> to determine the effect of neutralization of the waste on the soil capacity for Sr<sup>90</sup>.

The use of limestone for neutralizing the acidic waste was shown to inhibit substantially the soil uptake of strontium. If the limestone treatment is omitted, the soil column capacity more than doubles. The use of sodium hydroxide for neutralization in place of limestone, however, increases the soil capacity by a factor greater than 20.

In a previous Review<sup>1</sup> a description was given of a field test to be carried out on the storage of wastes in salt deposits. Oak Ridge has reported further progress on this subject.<sup>14</sup> Eight tests are planned requiring 11 excavations. Each test will run for approximately six months. The overall field test program will require about two years. Major variables to be studied include:

1. Type of waste.
2. pH.
3. Geometrical configuration of the cavity.
4. Surface area/volume ratio.
5. Method of construction.
6. Rate of heat production.

After an inspection of all the operating mines in the northeastern quadrant of the country, the Carey mine at Hutchinson, Kans., was chosen from among those willing to harbor the experiments. The decision to use the Carey mine was based on the geology, geographic location, facilities in the mine, estimated costs, and the possible location of future tests. The tests will begin in an unoccupied section of the mine in July 1959.

Temperature calculations on the storage of waste solutions as liquids in spherical cavities in salt show that for a 10-ft-diameter sphere and one-year-old waste the maximum rise in

temperature at the center of the sphere is 530°F at 1000 hr and 315°F at the surface of the sphere at 1500 hr. The maximum temperature rise for six-year-old waste at the center of the sphere is 100°F at 4500 hr and 65°F at the surface at 7000 hr. It is concluded that the thermal problem in salt disposal will cause no serious difficulties if the size of the cavities and the age and dilution of wastes are controlled.

Laboratory tests show that the structural properties of rock salt are not greatly altered by high radiation doses, although high temperatures increase the creep rate for both irradiated and unirradiated samples. Chemical interaction of liquid wastes with salt produced chlorine and other chlorine compound gases, but the volumes are not excessive. The migration of nuclides through the salt and deformation of the cavity can only be studied in the field.

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# PRODUCTION OF URANIUM, THORIUM, PLUTONIUM, AND THEIR COMPOUNDS

Improved methods are continually being sought for the preparation of feed materials for nuclear reactors and for reconversion of recovered fertile and fissile elements into forms suitable for reuse. The following paragraphs summarize developments in the production of intermediate compounds and the reduction of these intermediates to metallic form.

## *Uranium Tetrafluoride*

Current methods of producing uranium tetrafluoride in large tonnages involve contacting uranium dioxide with hydrogen fluoride at elevated temperatures in a countercurrent continuous system. Efforts to improve the process have centered upon: (1) the exploration of new types of processing equipment, primarily to improve gas-solid contact, temperature control, and heat removal; (2) the development of feeds from which uranium dioxide of greater reactivity toward hydrofluorination may be derived.

Uranium dioxide of very high reactivity can be made by precipitation of ammonium diuranate followed by calcination and hydrogen reduction. This method had been considered less desirable than the current process which involves thermal decomposition of uranyl nitrate because there are more process steps and because the product has a low bulk density. However, improvements in techniques under development at Fernald, Ohio, show promise of overcoming these disadvantages.<sup>1</sup> The greater reactivity of the uranium dioxide produced by the ammonium diuranate (ADU) process may reduce unit cost by allowing the use of a small excess of hydrogen fluoride.<sup>2</sup> Also the cost of operating and maintaining the denitration "pots" is high enough to justify development of alternative processes.

Following the development of a satisfactory ADU precipitation process on a laboratory and pilot-plant scale,<sup>3</sup> a semiworks facility was installed. This semiworks plant (Fig. 12), capable of producing one ton of ADU per day, has

been operated with only minor process interruptions during an eight-week period. The ammonium-to-uranium weight ratio to produce the desired pH of 5.7 averaged 0.165. The precipitate was of good quality with respect to filterability (213 gal/(sq ft)(hr) and tapped density (2.31 g/cc) of dried product. Calcination of the dried product in an indirect-fired Bartlett Snow calciner at a maximum gas temperature of 430 to 480°C produced a uniformly reactive product with an average tapped density of 2.55 g/cc. A twenty-fold reduction of sodium impurity in the uranyl nitrate fed to the process was demonstrated. Laboratory and production plant data have shown that sodium in uranium trioxide results in lower reduction (to uranium dioxide) and hydrofluorination (to uranium tetrafluoride) rates, lower plant on-stream time, and lower product (uranium tetrafluoride) assay.<sup>4</sup>

To determine the susceptibility of ADU to thermal damage, surface area measurements were made on samples heated for 30 min at various temperatures. The results, given in

Table V-1 SURFACE AREA OF PILOT PLANT ADU  
AFTER HEATING AT VARIOUS TEMPERATURES<sup>1</sup>

Heating time: 30 min

Temp., °C	Specific surface area, sq m/g*
110†	4.5
349	4.3
454	12.1
538	15.3
593	10.5
649	5.6
704	2.4
760	1.0

\*Determined by nitrogen adsorption method.

†Heated for 28 hr.

Table V-1, showed that a large increase in surface area occurred on heating between 450 and 600°C; above this temperature thermal

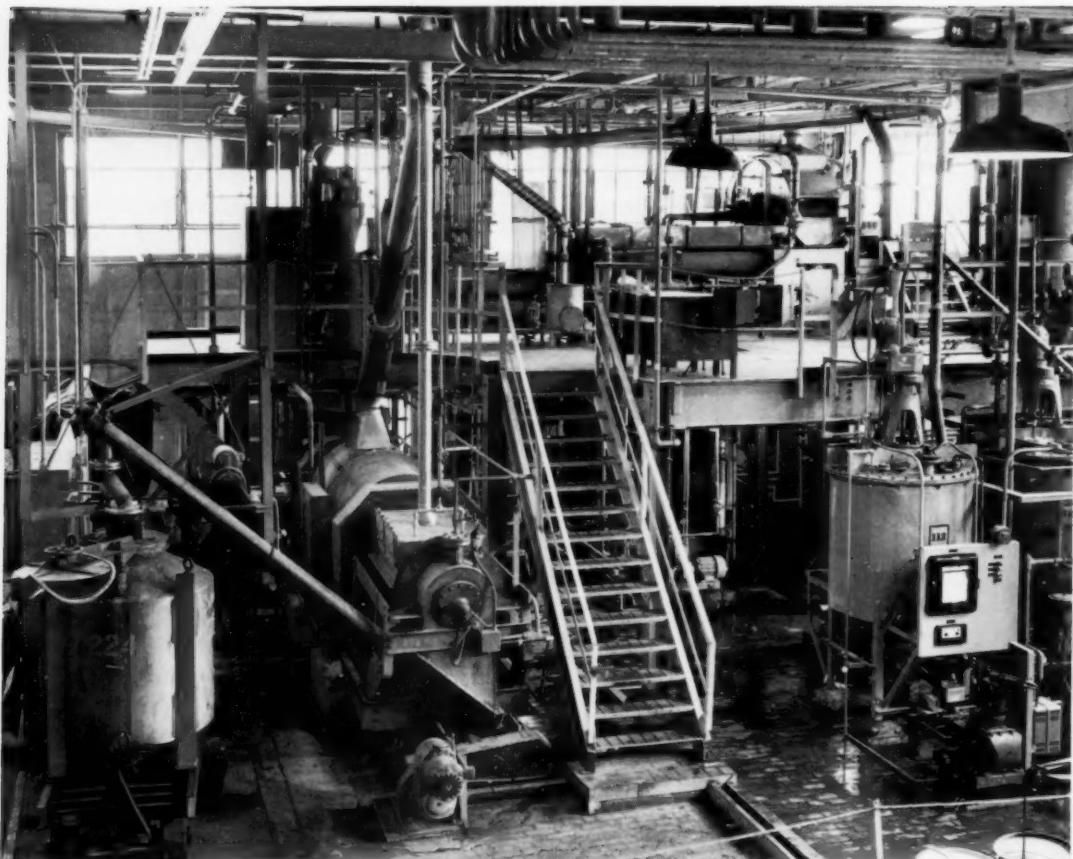


Figure 12—Ammonium diuranate process semiworks pilot plant.<sup>1</sup>

damage occurred. Two exothermic transitions were detected by differential thermal analysis at 350 to 450°C during calcination, which apparently are responsible for the increase in surface area.

Full-scale plant tests of fluid-bed reduction and screw-reactor hydrofluorination indicated a high level of performance for the ADU source feed (based on preliminary results). Lot samples showed high (97.1 per cent) conversion to uranium tetrafluoride with an 8 per cent excess of hydrogen fluoride. The green salt produced during this brief full-scale operation was reduced to uranium metal by the standard process. Separation of slag and metal was unusually good. Yields and quality of metal were equivalent to

those experienced with green salt produced by the conventional process.

Forty tons of calcined ADU is being prepared in the semiworks facility for more complete evaluation in the green salt plant.

### *Thorium*

Over the last ten years the interest in thorium as a fertile material for nuclear reactors has fluctuated considerably. At present the interest in thorium has again waned, but as a result of earlier interest a considerable amount of AEC-sponsored development work has been done on thorium production processes. The following summarizes briefly the status of development and small-scale production.

The main source of thorium is monazite sand in which rare-earth compounds are important by-products. The "opening up" of the monazite sands to yield crude thorium and rare-earth fractions has been done by either a sulfuric acid or a caustic soda method.<sup>5</sup> These are essentially leaching and precipitation processes. For nuclear use, high purification is required and solvent extraction refining procedures have proved most effective. A refining process using tributyl phosphate in a hydrocarbon solvent has been demonstrated on a pilot-plant scale using pump-mix mixer-settler units.<sup>6</sup> This study indicated that an aliphatic hydrocarbon diluent, such as a refined kerosene, gave somewhat poorer separation from rare earths than did an aromatic diluent. The diluent chosen was "Solvesso-100," an aromatic solvent boiling in the range of 158 to 176°C.

The basic thorium metal reduction process used by the AEC was developed at the Ames Laboratory of Iowa State College, and until 1954 all metal production was at this site. Briefly, the Ames process consists in precipitating thorium oxalate by the addition of oxalic acid or ammonium oxalate to a solution of acidified thorium nitrate. The oxalate precipitate is filtered, washed, dried, and then calcined in an oxidizing atmosphere. The oxide is hydrofluorinated at about 550°C with anhydrous hydrogen fluoride.<sup>7</sup> The thorium fluoride is mixed with high-purity redistilled calcium and anhydrous zinc fluoride and fired in a steel reduction bomb, lined with electrolytically fused dolomite. A biscuit (weighing about 50 lb) of a relatively low melting alloy of thorium and zinc forms at the bottom of the bomb. It is subsequently subjected to a vacuum distillation at 1100°C to remove the zinc. The thorium sponge which remains is melted by induction heating in a beryllia crucible and cast into a graphite mold using a bottom-pouring technique. It is then cast into ingots approximately 3½ in. in diameter and 36 in. long weighing about 100 lb.

In 1954, a thorium pilot plant was placed in operation at Fernald, Ohio. A number of modifications of the Ames process were tried in this pilot plant most of which did not prove successful. However, consumable electrode arc-melting of dezinced thorium biscuits proved to be a much more satisfactory method than induction melting for ingot production. Ingots 7 in. in diameter and weighing approximately 400 lb were produced.

In addition to the processes used at Ames and Fernald, development work has been done on five alternate reduction methods. These methods and the sites performing the work are as follows:

1. Electrolytic reduction of thorium tetrachloride<sup>8</sup> (Horizons, Inc.).
2. Magnesium reduction of thorium tetrachloride<sup>9,10</sup> (Bureau of Mines and Ames Laboratory).
3. Sodium reduction of thorium tetrachloride<sup>11</sup> (Oak Ridge National Laboratory).
4. Calcium reduction of thorium oxide<sup>12</sup> (Sylvania Electric Products, Inc.).
5. Electrolytic reduction of thorium oxide<sup>13</sup> (Savannah River Laboratory, DuPont Company).

Three of the five methods involve the use of thorium tetrachloride as a starting material, and two involve the use of thorium oxide. None of the processes results in massive thorium but rather in metal ranging from a very fine powder to a porous sponge. The oxide reduction with calcium appears to be the cheapest and simplest, but the resulting finely divided powder may be hazardous. All of the five processes appear capable of producing thorium metal as satisfactory as that produced by the calcium reduction of the fluoride, at least with respect to over-all chemical purity.

The quality of thorium metal, with respect to its suitability for nuclear reactor use, has been studied and recently reported.<sup>14</sup> A low thorium oxide content is one of the most important requirements of reactor-grade thorium. Preferred methods of fabrication of several shapes of thorium elements, particularly coextrusion, require a clean soft metal, and thorium oxide seems to be one of the factors contributing to the hardness of the metal. The thorium oxide is insoluble in most solvents and if undissolved would result in product losses in the separation process for the isolation of U<sup>233</sup>. The only metal that has been produced to date on a substantial scale is that produced by the consumable electrode arc-melting process at Fernald. It has a satisfactory oxide content (less than 1 per cent) and a hardness level suitable for extrusion. It is considered suitable for any type of reactor irradiation. Production experience with arc-melted metal has shown that the recommended limits on chemical impurities can be met.

No large-scale thorium production plants have yet been placed in operation, but sufficient knowledge is at hand if the need arises.

## Uranium

### $U^{233}$ Purification and Metal Production

Since 1953, kilogram quantities of  $U^{233}$  have been routinely processed to metal at the Los Alamos Scientific Laboratory. It is obtained from the Oak Ridge Thorex pilot plant, in which  $U^{233}$  is separated from thorium and fission products by dissolution and solvent extraction of irradiated thorium slugs. The end product of the Thorex process is a uranyl nitrate solution low in fission products and contaminating cations.<sup>15</sup>

The handling of  $U^{233}$  is much more difficult than the handling of  $U^{235}$  because of the presence of large amounts of alpha and beta-gamma activity. For the isotopic mixtures usually encountered,  $U^{233}$  has a specific alpha activity 150 times as large as  $U^{235}$  ( $Pu^{239}$  is 50 times more active than  $U^{233}$ ). With respect to beta-gamma activity, nearly all of the activity stems from  $U^{232}$  present as a contaminant in the  $U^{233}$  to the extent of about 10 to 40 ppm. The half-life of  $U^{232}$  is 74 years, and the short half-lives of its daughters contribute to a rapid growth of beta-gamma activity making the handling of  $U^{233}$  difficult.

Since it is not possible to separate the  $U^{232}$  from the  $U^{233}$ , the only effective procedure for reducing beta-gamma activity is in separation of the immediate daughter,  $Th^{228}$ . The  $Th^{228}$  daughters, for lack of a parent, die off with the 3.64-day half-life of  $Ra^{224}$  until the  $Th^{228}$  again grows in. The activity thus decreases for a period ranging from several days to about three weeks, depending on the  $U^{232}$  content.

Using a cation-exchange operation, the objectionable  $Th^{228}$  is quantitatively removed from the uranium along with some undetermined fraction of the  $Th^{228}$  daughters.<sup>16</sup> A four-section drybox (Fig. 13) shielded with a 4-in.-thick boiler plate permits an operator to handle two batches per day at 2 r/hr radiation level each. The windows are 2-in.-thick leaded glass. Equipment within the box provides means for evaporation of excess acid from the feed solutions, followed by filtration, volume adjustment, sampling, ion exchange, and the dissolution and recycling of scrap from various operations. This shielded box is in no sense a remote operation, but nearly all transfers are accomplished by vacuum, and the routing of the solutions is accomplished by connection of appropriate semiball joints and

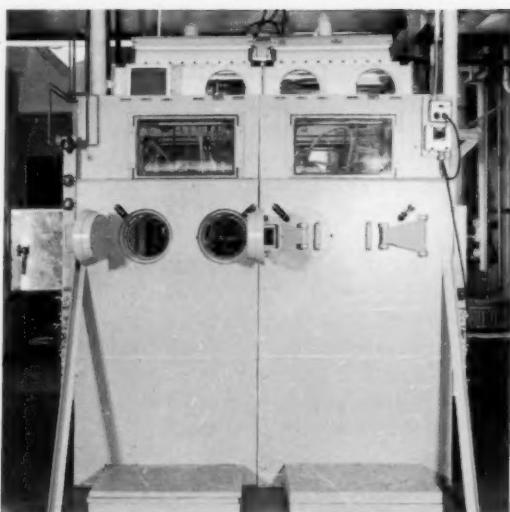


Figure 13—Four-section shielded drybox for removal of  $Th^{228}$  from  $U^{233}$  by cation exchange.<sup>16</sup>

flexible tubing. The only time an operator need be in or near the box is while making connections or turning valves.

In all the operations with  $U^{233}$ , nuclear safety requirements are met by limiting the batch size to 250 g. The dryboxes have wells built into the floor to accommodate the process glassware and to prevent combination of several batches in the event of breakage. Specific, limited locations are provided for each solution handled to reduce the probability of inadvertently having more material than is nuclearly safe in any one box.

After reduction of beta-gamma activity by removal of  $Th^{228}$ , the  $U^{233}$  can be processed in unshielded dryboxes of conventional design. The purification is accomplished by precipitation of  $UO_4 \cdot xH_2O$  by the addition of hydrogen peroxide after pH adjustment. Redissolution and precipitation are usually required to attain the desired purity.

The final uranium peroxide is vacuum filtered on a platinum frit and calcined to uranium oxide at 800°C. The preparation of uranium tetrafluoride is accomplished in the usual manner by hydrogen reduction and hydrofluorination using a nickel boat in a nickel reactor. Conversion of uranium tetrafluoride to metal is done by the bomb reduction method after the addition of calcium and iodine. Yields average greater than 98 per cent, and total impurities average less than 500 ppm.

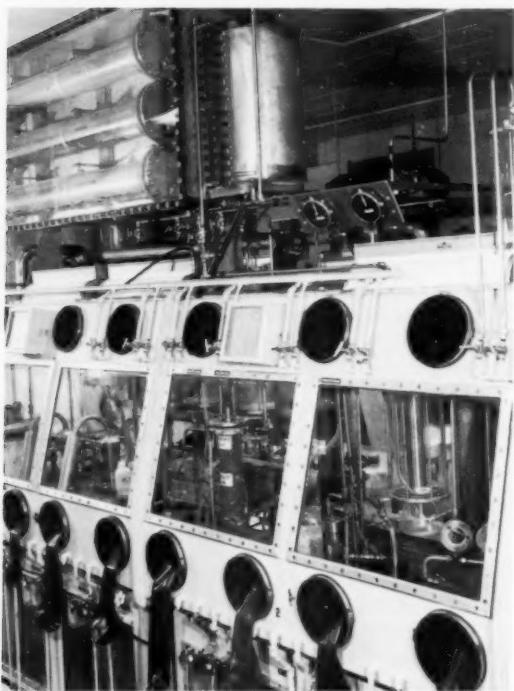


Figure 14—Uranium-233 solvent-extraction equipment.<sup>16</sup>

Scrap materials are recovered by solvent extraction. The equipment, consisting of dissolver, storage tanks, two 4-ft-long columns, and feed system, is built into a glove box as shown in Fig. 14. The concentrates from solvent extraction are returned for peroxide precipitation and eventual inclusion in recovery lots.

#### Continuous Production of Uranium Metal

A semicontinuous process to produce uranium metal by the reduction of uranium tetrafluoride with magnesium is being developed on a pilot scale at Fernald. Progress through 1957 was reviewed in a previous issue of this publication.<sup>17</sup> More recent developments<sup>1</sup> are discussed below.

Green salt-magnesium briquettes are fed from a conveyor into a stainless-steel tube located on top of a graphite reactor, heated at 1510°C and contained in a helium atmosphere. In the original method molten uranium was poured through the bottom of the reactor (by the use of a shear plug) into a graphite mold. The slag product was drawn through an overflow within the wall of the crucible and cast in a separate mold. Fre-

quent failure of pouring nozzles occurred due to oxidation of the graphite. A special two-way-pore induction furnace was found to be more satisfactory. With this unit, the feed briquettes were conveyed at a regulated rate (about 25 lb/min) and dropped through the top charging device into the reactor. Most of the magnesium fluoride slag formed was discharged by tilt-pouring from the rear spout of the furnace into a graphite mold. After reduction of all briquettes was completed, the reduction products were held for a short period to promote separation of the slag and metal. The charging device was then removed and the uranium tilt-poured into another graphite mold at the front of the furnace. Enough slag was poured with the uranium to protect the metal from oxidation.

Table V-2 EVALUATION OF EXCESS MAGNESIUM IN THE GREEN SALT-MAGNESIUM CHARGE<sup>1</sup>

No. of reductions	Excess Mg, %	Average reduction yield, %	Range of reduction yield, %	Remarks
3	2	92.4	87.9–95.8	Oxide penetration into the uranium
3	4	92.0	89.7–94.1	Oxide penetration into the uranium
3	6	96.1	93.2–100.2	

The effects of magnesium excess of 2, 4, and 6 per cent over the stoichiometric requirements were evaluated. Six per cent excess magnesium was judged best as shown in Table V-2. Casting yields have thus far been low (about 70 per cent) because some uranium did not pour from the furnace. Oxide has been found between the slag and uranium product in runs in which the products were allowed to solidify in the reactor. It is believed that these oxides prevented some of the uranium from pouring from the reactor.

Most of the test runs have been made with 180-lb batches of briquettes. The metal produced has contained 200 to 400 ppm carbon and 15 to 80 ppm nitrogen. Laboratory tests have indicated that magnesia-alumina spinel may be a satisfactory crucible material for this process.

Improved pilot-plant facilities have been installed including a sealed-atmospheric enclosure for the reduction equipment and materials handling equipment for charging the briquettes

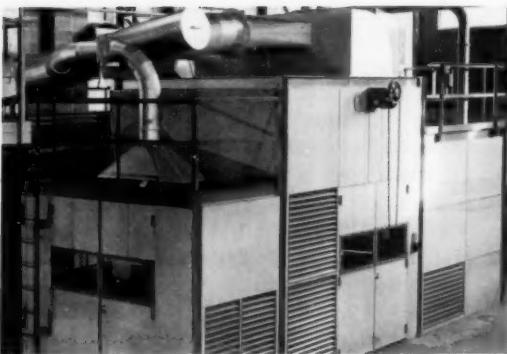


Figure 15—Enclosure for semicontinuous reduction equipment.<sup>1</sup>

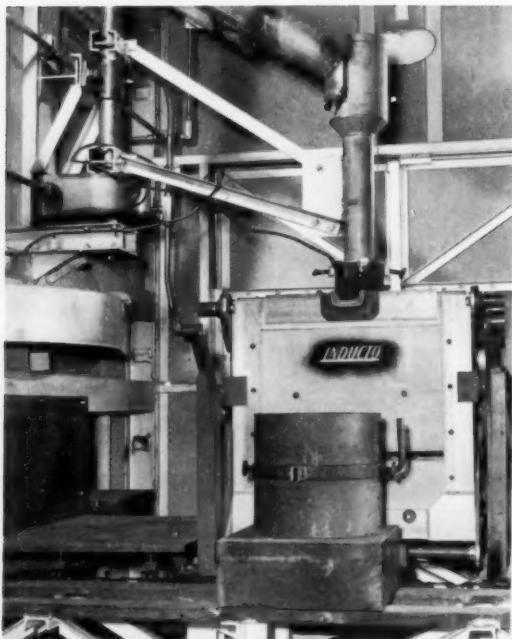


Figure 16—Semicontinuous uranium reduction furnace and auxiliary equipment.

and for other operations. Some of the pilot-plant facilities are shown in Figs. 15 and 16.

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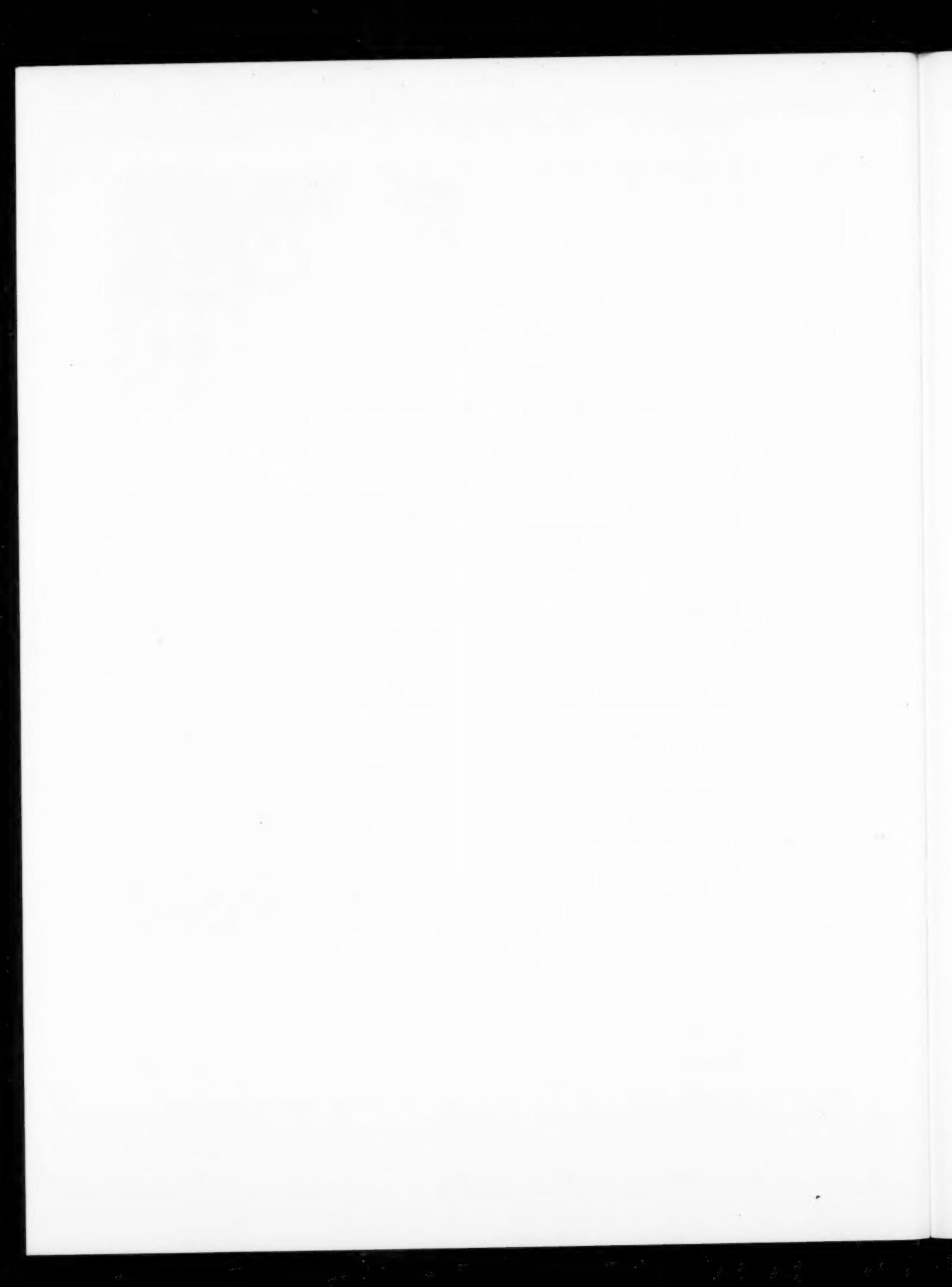
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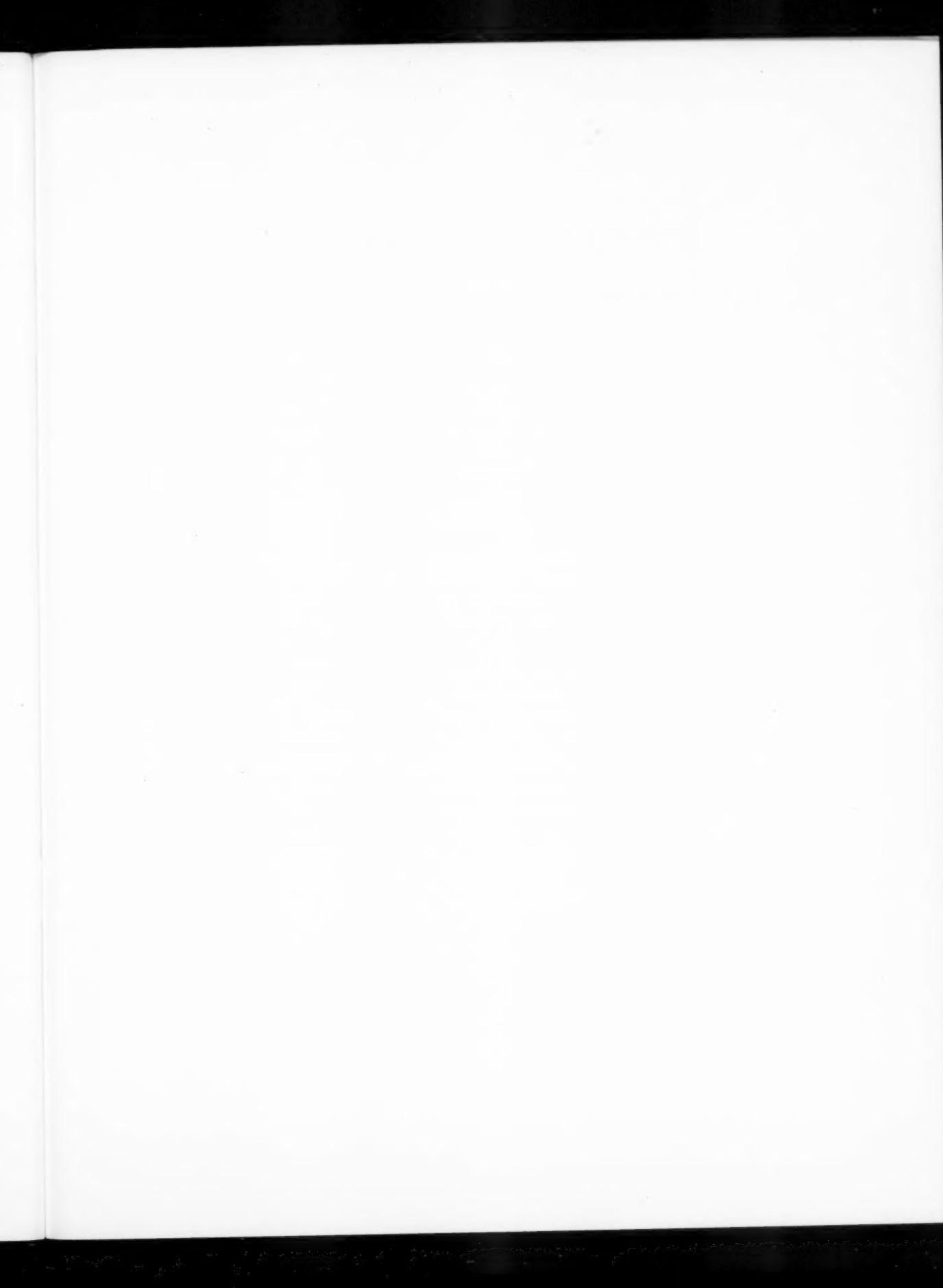
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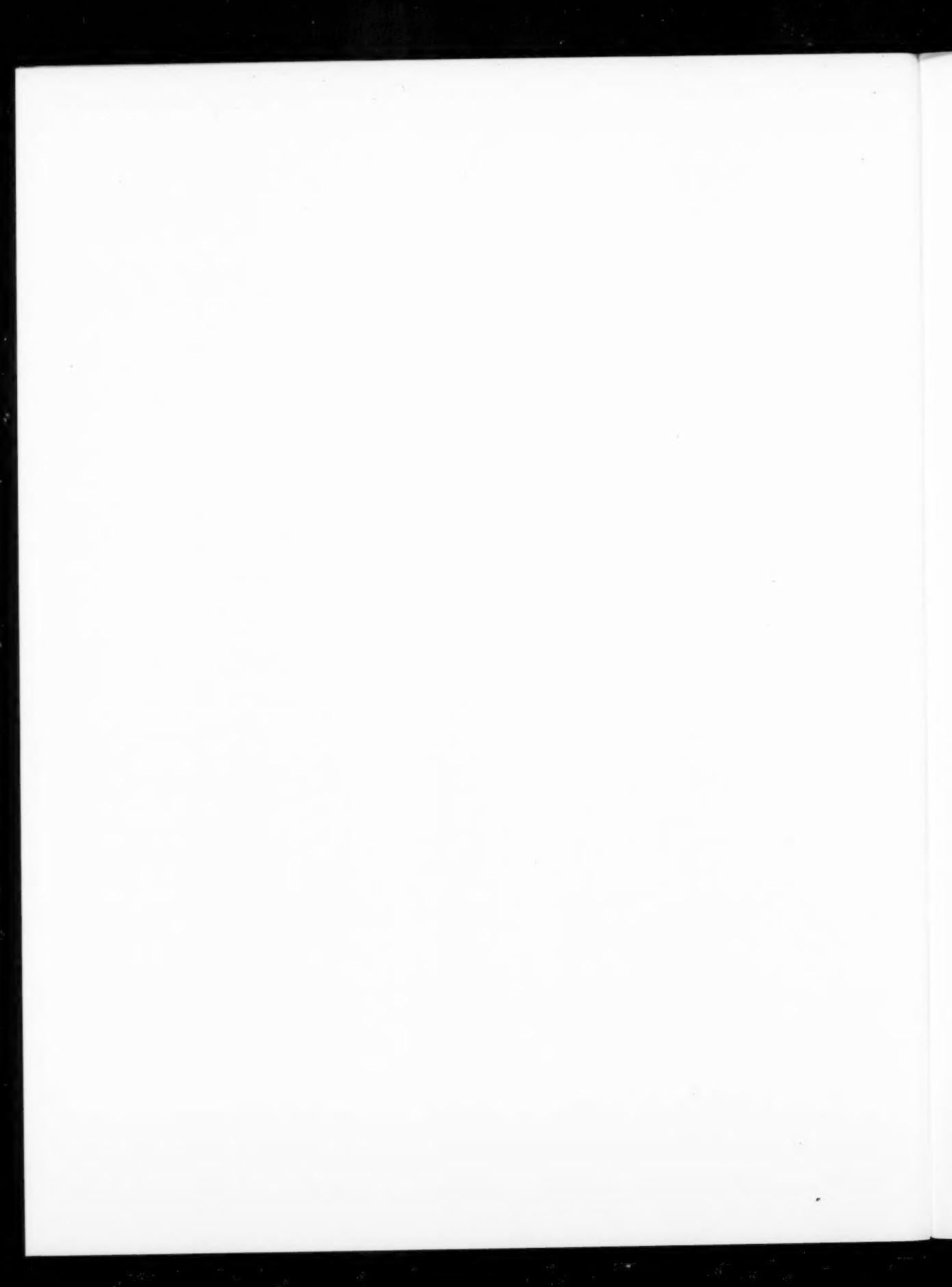
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